RIA-84-U214

HIGH ENERGY BINDERS
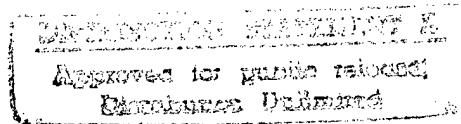
SUMMARY REPORT

January 1984

by: G. E. Manser, R. W. Fletcher, and G. C. Shaw

Prepared for:

OFFICE OF NAVAL RESEARCH

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The objective of this research was to develop the synthesis and polymerization of energetic and non-energetic monomers for use as binders in solid gun propellants, melt cast PBXs and cast-cured PBXs. The polymers are designed to meet the requirements of the Navy's LOVA (Low Vulnerability Ammunition) program. During this reporting period we have developed a series of azido, nitrate ester and mixed azido/nitrate ester urethane curable prepolymers. Initial evaluation reveals that these polymers meet thermal and chemical stability criteria for continued study.

We have synthesized alternating crystalline and amorphous block copolymers, based on non-energetic cyclic ether monomers, that exhibit thermoplastic elastomer behavior. The melting point transition (working)

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18. (cont) monomer synthesis   lymer synthesis, reactivity ratio, binder properties, functi   ity.

19. (cont) temperature meets   e program goals of 90°C. The resulting melt cast polymer showed the typical tough, high modulus properties of thermoplastic elastomers with a low melt viscosity at projected formulation temperatures. Physical integrity is maintained to within 5°C of the working temperature. These polymers exhibit endothermic decomposition/depolymerization at elevated temperatures.

The determination of reactivity ratios of monomer pairs was continued. Information thus gathered was used to select new monomer structures for synthesis and to enable selection of monomer pairs that yield polymers of low crystallinity. Analytical procedures and a computer program were developed for this work.

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ACKNOWLEDGEMENTS

I. INTRODUCTION AND BACKGROUND

The object of this research was to develop new binder systems for Navy applications. In our previously reported research (Ref 1) we developed a series of azido polyether glycols that fulfilled the requirements of a binder system with a high heat of formation, and the first in a series of thermoplastic elastomers that would meet the Navy's LOVA gun propellant program (Ref 2). Because of the obvious similarities in both programs we have combined them and continued to develop new binder systems.

Energy is derived from the introduction of azido, nitrate ester, nitro, and nitramine groups into preformed cyclic ether monomers. As a result of our earlier work we had developed a method wherein we could control the polymerization of cyclic ether monomers to produce polymers for DoD binder applications (Ref 3). Our work on the azido class of polymers was completed and we turned our attention to the synthesis of nitrate ester polyethers.

In our earlier work on the synthesis of thermoplastic elastomers we had demonstrated that the use of our techniques, adapted to the synthesis of block copolymers, produced materials that would fulfill the objectives of the LOVA program. The materials produced had a working (extrusion) temperature in the required temperature range and the polymers exhibited an endothermic decomposition at 300°C. In order to lower the melt viscosity, decomposition temperature, and optimize physical properties, we continued our research.

II. DISCUSSION

The deficiencies of current gun propellant binders, melt cast explosives, PBXs, and solid rocket propellants may be overcome by the use of thermoplastic elastomers. The current state-of-the-art formulations have serious problems that include, but are not limited to, use of nonenergetic binders, high end-of-mix viscosities, thermally labile urethane linkages, and extreme vulnerability to unscheduled detonation.

With this in mind we embarked on a research program that would, in the long term, develop a new generation of binders specifically for DoD applications. We recognized that different applications would require special binders. Gun propellant binders would not meet the requirements of melt cast explosives, but the chemistry required to synthesize both would be similar enough that modifications of the basic materials would allow the synthesis of each particular material. Another obvious point was that although we believe that thermoplastic elastomers could be the mainstay of future formulations, urethane curable systems will continue to be used for a considerable time. Therefore, we have continued to develop energetic polyether glycols that are isocyanate curable.

The materials which we have and will continue to develop on this program must meet certain physical and chemical standards. In order to be considered for further evaluation they must:

1. Be chemically stable from -40° to 60°C
2. Be able to increase the energetic nature of the formulation
3. Be processible in state-of-the-art equipment
4. Be compatible with existing formulation components
5. Retain mechanical integrity when filled with solids up to 80 weight percent
6. Exhibit endothermic depolymerization at temperatures above 120°C but below that of the autoignition temperature of the oxidizer
7. Have a Tg below -40°C

84589-4.6

As stated above we are developing two discrete types of binder systems, energetic polyether glycols and thermoplastic elastomers. Although these materials may be considered somewhat different in nature the chemistry to produce each is similar using the same class of monomers. It is only in the final stages of the synthesis that different techniques are used.

Our research therefore has been conducted via the following subtasks:

1. Monomer synthesis
2. Polymer synthesis
3. Polymer characterization
4. Polymer evaluation
5. Formulation
6. Kinetic studies

For the purpose of this document we will report each task in the order given.

MONOMER SYNTHESIS

The monomers used in our research are all classified as cyclic ethers, each one specifically synthesized for predetermined use in the program. Some are intermediates, some nonenergetic, and some energetic. The actual uses of each will be discussed in the polymer synthesis portion of this report.

3,3-Bis(ethoxymethyl) oxetane (BEMO)

BEMO is prepared by the action of sodium ethoxide, in ethanol on 3,3-Bis(chloromethyl) oxetane (BCMO).
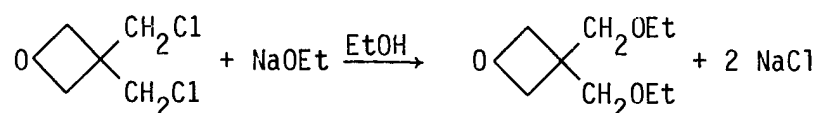
$$\text{BCMO} \left(CH_2Cl, CH_2Cl \right) + NaOEt \xrightarrow{EtOH} \left(CH_2OEt, CH_2OEt \right) + 2\,NaCl$$

The monomer is obtained in high yield and polymerizable purity by vacuum distillation.
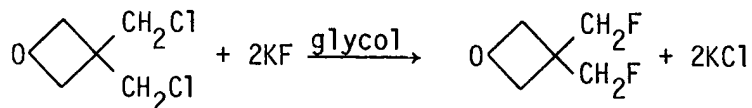
3,3-Bis(methoxymethyl) oxetane (BMMO)

BMMO is prepared by the action of sodium methoxide, in methanol on BCMO.
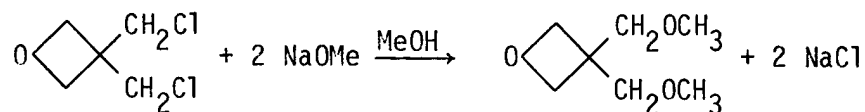
$$\left(CH_2Cl, CH_2Cl \right) + 2\,NaOMe \xrightarrow{MeOH} \left(CH_2OCH_3, CH_2OCH_3 \right) + 2\,NaCl$$

The monomer is obtained in high yield and polymerizable purity by-vacuum distillation.

3,3-Bis(fluoromethyl) oxetane (BFMO)

BFMO is prepared by the action of potassium fluoride, in ethylene glycol on BCMO.

$$\left(CH_2Cl, CH_2Cl \right) + 2KF \xrightarrow{glycol} \left(CH_2F, CH_2F \right) + 2KCl$$

The monomer is obtained in moderate yield and polymerizable purity by vacuum distillation.

3-Hydroxymethyl-3-methyl oxetane (HMMO)

HMMO is prepared by the action of diethylcarbonate on tris(methylol) ethane. The cyclic carbonate is thermally decomposed at 160°C and HMMO is obtained by subsequent distillation from the reaction products. Polymerizable purity monomer is obtained in high yield by redistillation.

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$$CH_3-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH \ + \ \overset{\displaystyle CH_3CH_2-O}{\underset{\displaystyle CH_3CH_2-O}{\diagup}}C=O \quad \xrightarrow[-2C_2H_5OH]{\Delta \ Cat.}$$

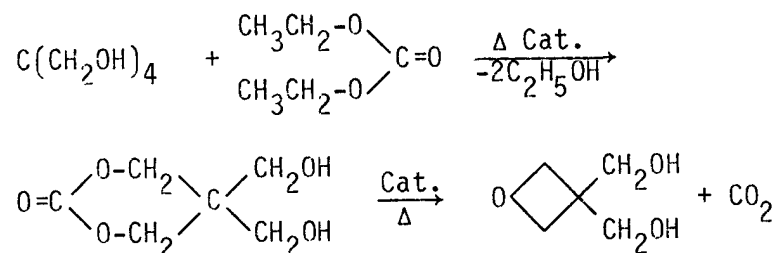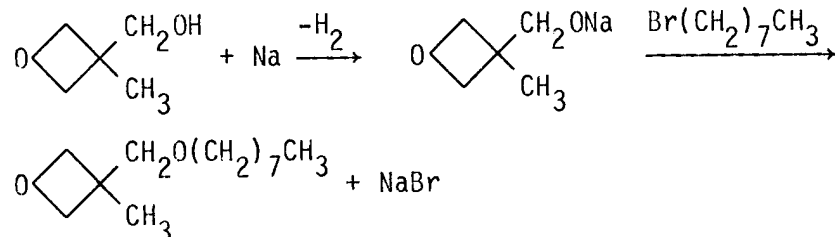$$O=C\overset{\displaystyle O-CH_2}{\underset{\displaystyle O-CH_2}{\diagup\diagdown}}C\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_3}{\diagup\diagdown}} \quad \xrightarrow[\Delta]{Cat.} \quad O\diamond\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_3}{}} \ + \ CO_2$$
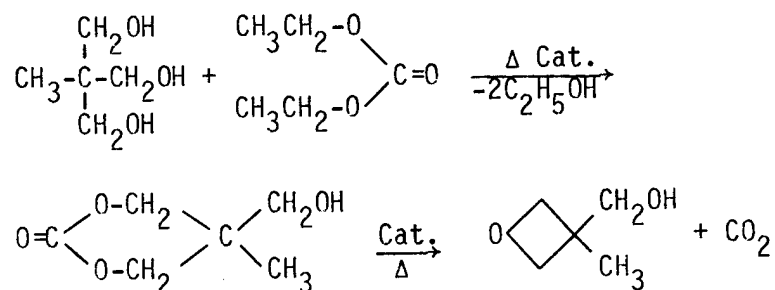
3,3-Bis(hydroxymethyl) oxetane (BHMO)

BHMO is prepared by the action of diethylcarbonate on pentaerythritol. The cyclic carbonate is thermally decomposed at 140°C and BHMO is obtained by subsequent distillation from the reaction products. Polymerizable purity monomer is obtained in moderate yield by redistillation.
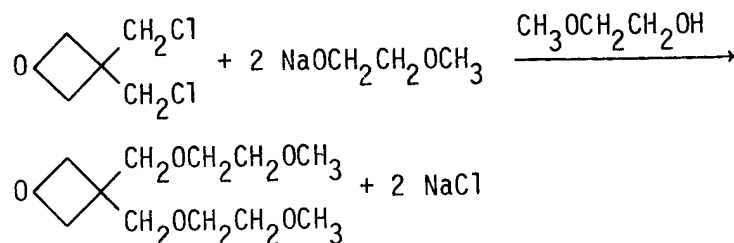
$$C(CH_2OH)_4 \ + \ \overset{\displaystyle CH_3CH_2-O}{\underset{\displaystyle CH_3CH_2-O}{\diagup}}C=O \quad \xrightarrow[-2C_2H_5OH]{\Delta \ Cat.}$$

$$O=C\overset{\displaystyle O-CH_2}{\underset{\displaystyle O-CH_2}{\diagup\diagdown}}C\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{\diagup\diagdown}} \quad \xrightarrow[\Delta]{Cat.} \quad O\diamond\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{}} \ + \ CO_2$$

3-Octoxymethyl-3-methyl oxetane (OMMO)

OMMO is prepared by the action of bromooctane on the sodium salt of HMMO. The sodium salt of HMMO is prepared by dissolving sodium in a solution of HMMO in dioxane at room temperature. The required OMMO is isolated from the precipated sodium bromide by filtration. Subsequent distillation affords the monomer in moderate yield at polymerization purity.

$$O\diamond\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_3}{}} \ + \ Na \ \xrightarrow{-H_2} \ O\diamond\overset{\displaystyle CH_2ONa}{\underset{\displaystyle CH_3}{}} \ \xrightarrow{Br(CH_2)_7CH_3}$$

$$O\diamond\overset{\displaystyle CH_2O(CH_2)_7CH_3}{\underset{\displaystyle CH_3}{}} \ + \ NaBr$$

3,3-Bis(methoxyethoxymethyl) oxetane (BMEMO)

BMEMO is prepared by the action of the sodium salt of 2-methoxyethanol on BCMO in excess 2-methoxyethanol. The monomer is obtained in high yield by vacuum distillation at polymerizable purity.
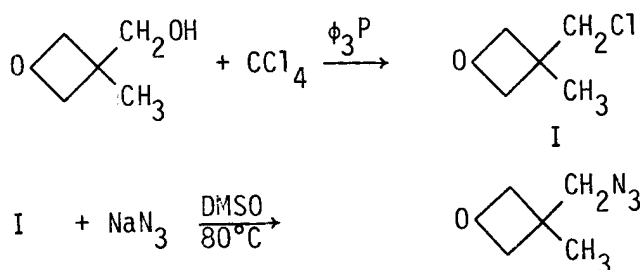
$$0 \underset{CH_2Cl}{\overset{CH_2Cl}{\diamond}} + 2\ NaOCH_2CH_2OCH_3 \xrightarrow{CH_3OCH_2CH_2OH}$$

$$0 \underset{CH_2OCH_2CH_2OCH_3}{\overset{CH_2OCH_2CH_2OCH_3}{\diamond}} + 2\ NaCl$$

3-Chloromethyl-3-methyl oxetane (CMMO)

CMMO was synthesized as a useful intermediate oxetane monomer. Many of our monomers are prepared by the reaction of the sodium salts on alkyl halides and as a result the yields are low. This is a result of the limitations inherent in the formation of the sodium salts of cyclic ether alcohols, and a limited number of suitable solvents. Previously we attempted the synthesis of CMMO by reaction of HMMO with various agents, thionyl chloride, etc., but these methods always resulted in a competitive ring opening reaction. Recently we have developed the successful synthesis of CMMO by reaction of carbon tetrachloride on HMMO in the presence of triphenyl phosphine.

$$0 \underset{CH_3}{\overset{CH_2OH}{\diamond}} + CCl_4 \xrightarrow{\phi_3 P} 0 \underset{CH_3}{\overset{CH_2Cl}{\diamond}}$$
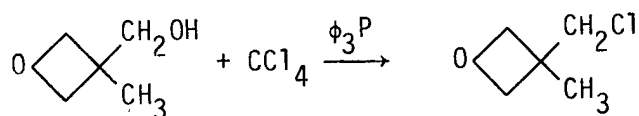
As a result of this synthesis we can now report an alternative route to 3-azidomethyl-3-methyl oxetane (AMMO), a monomer synthesized by us four years ago. The original synthesis of AMMO was based on the formation of the tosylate of HMMO and subsequent reaction of it with sodium azide. Our original work suggested that the tosylate should be isolated but the recent work of Frankel (Ref 4) has resulted in a technique whereby it is not necessary to isolate the intermediate. By this latter method AMMO is being prepared in large quantities and excellent yields. Although an economic study has not yet been made, we offer this total synthesis of AMMO.

$$0 \underset{CH_3}{\overset{CH_2OH}{\diamond}} + CCl_4 \xrightarrow{\phi_3 P} 0 \underset{CH_3}{\overset{CH_2Cl}{\diamond}}$$
$$\text{I}$$

$$\text{I} + NaN_3 \xrightarrow[80°C]{DMSO} 0 \underset{CH_3}{\overset{CH_2N_3}{\diamond}}$$

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Obviously, CMMO can be competitively used in the synthesis of OMMO and other monomers that use HMMO.

3,3-Bis(nitratomethyl) oxetane (BNMO)

BNMO is readily prepared by the action of acetyl nitrate on BHMO. The monomer is isolated from the reaction mixture by extraction and recrystallization from carbon tetrachloride. A further recrystallization yields the monomer in polymerizable grade purity.
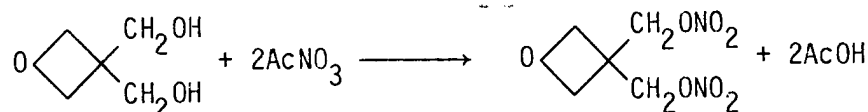
3-Nitratomethyl-3-methyl oxetane (NMMO)

NMMO is readily prepared by the action of acetyl nitrate on HMMO. The monomer is isolated by extraction of the reaction products and may be purified by column chromatography or distillation at room temperature. Either method yields NMMO in high yield and polymerizable purity.
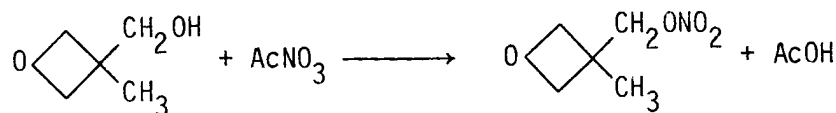
A more detailed account of each synthesis is given in the experiment portion of this report.

POLYMER SYNTHESIS

In our previous work (Ref 3) we had demonstrated a new polymerization technique that would yield polyether glycols of a preselected molecular weight, functionality, and narrow polydispersity. We had demonstrated that, in general, copolymers and terpolymers yield superior mechanical properties when compared with those of homopolymers. By this technique we had synthesized a series of azido polymers that showed numerous applications for use in explosive formulations. These polymers are now being scaled up and distributed to various laboratories. Therefore, the following polymers can be considered state-of-the-art and available for use:

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1. Poly (BAMO)

2. Poly (AMMO)

3. Poly (AZOX)

4. Poly (BAMO/THF)

5. Poly (BAMO/AMMO)

6. Poly (BAMO/AZOX)

7. Poly (AMMO/THF)

8. Poly (AMMO/AZOX)

9. Poly (AZOX/THF)

We have evaluated each polymer system and the exploratory research can be considered completed.

For the purpose of our ongoing research we divided the polymer synthesis into three parts:

1. Synthesis of energetic polymers
2. Synthesis of nonenergetic polymers
3. Synthesis of block polymers (thermoplasic elastomers)

1. SYNTHESIS OF ENERGETIC POLYMERS

This portion of our work was directed towards the synthesis of a new series of energetic polyether glycols, namely nitrato ester polyether glycols. Although the azido polymers can be considered energetic, due to the high heat of formation of the polymer, they lack the energetic oxygen content of nitro, nitrato, and nitramine polymers. Therefore we synthesized a new generation of nitrate ester polymers. As a result of our monomer sythesis effort we had available to us the monomers Bis(nitratomethyl) oxetane (BNMO) and nitratomethyl methyl oxetane (NMMO). These monomers and BAMO were used to form three polymers. The reason we included the azido monomer was to synthesize a nitrate ester polymer with a positive heat of formation. We prepared the following polymers,

1. Poly (BAMO/BNMO)
2. Poly (BNMO/NMMO)
3. Poly (NMMO)

Each polymer was synthesized by our polymerization technique to a molecular weight of 5,000 and at various functionalities (2 to 2.5). We found that solution polymerization carried out at 0°C using butanediol/boron trifluoride etherate (Ref 3) produced the required polymers in conversion of over 90%. Poly (NMMO) is a mobile liquid at room temperature whereas poly (BAMO/BNMO) and poly (BNMO/NMMO) are waxes which melt at approximately 25°C. Due to the nature of the nitrate ester group each polymer could not be precipitated by methanol but using mixed solvents such as hexane/propanol yielded polymers without residual unreacted monomer. Column chromatography could be used as a purification step by elution through an alumina column with methylene chloride.

2. SYNTHESIS OF NONENERGETIC POLYMERS

This research was directed towards the synthesis of polymers specifically for subsequent use in preparing the thermoplastic elastomers.

Thermoplastic elastomers are block copolymers with the property of forming physical crosslinks at predetermined temperatures. The classical TPE obtains this property by having one of the component block's glass point above room temperature (KRATON). Thus at temperatures below 100°C the glassy block forms glassy domains in the polymer and thus physically crosslinks it. We proposed to form TPEs from polyether glycols that have similar properties but that would derive the physical crosslinking from the formation of crystalline domains. It is significant to replace the amorphous glassy blocks with crystalline blocks. Basic thermodynamic incompatibility between the two blocks is not required for phase separation because of the heat of fusion of the crystalline block. Another advantage may be the increased solvent resistance of the crystalline block. Perhaps the most important advantage of the crystalline block is that the melt viscosity will decrease more rapidly on increasing temperature above the melting point of the crystalline block.

Therefore we embarked upon the synthesis of two distinct series of polyether glycols:

  1. Polymers that were crystalline in nature with melting point temperatures of 80° to 90°C

  2. Polymers that were amorphous in nature with glass transition temperatures of less than -40°C

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From our previous work (Ref 2) we had synthesized poly (BEMO) which had the nearly ideal crystalline properties we were looking for. Subsequently we have synthesized poly (BMMO) and observed almost identical properties. Both these homopolymers melt at 80° to 90°C; however, poly (BMMO) has a higher ether oxygen content than poly (BEMO) which could be advantageous. We have also synthesized poly (BFMO) in order to observe its physical properties and gage its potential usefulness. We found that poly (BFMO) has a melting point of 105°C which may be applicable where a higher melting point may be neces- sary. Obviously poly (BFMO) has a higher density than poly (BEMO) and poly (BMMO) which again may suit particular applications. Each of these polymers was prepared by our reported procedure and was isolated by methanol precipi- tation.

For use as soft block polymers we concentrated on the synthesis of co- polymers based on poly (tetrahydrofuran). We synthesized these polymers be- cause poly (THF) has a very low Tg and we found that THF/oxetane copolymers formed good elastomers with the potential of being ideal amorphous blocks for our TPEs. We divided this work into two phases:

1. Copolymers of THF and simple oxetane monomers
2. Internally plasticized THF polymers

Three copolymers of THF were synthesized. These consisted of:

1. THF/BEMO
2. THF/BMMO
3. THF/BFMO

Each polymer was synthesized to varying molecular weights and monomer ratios. The ability of the TPE to phase separate is dependent on the mutual incompatibility of the individual blocks. This may be caused by the chemical nature of the component blocks or merely by physical size. Theoretical cal- culations revealed that if we synthesized a block of poly (BEMO) to 20,000 molecular weight then a block copolymer of THF/BMMO would need to be 35,000 to 45,000 in order to phase separate. Therefore we synthesized copolymers of THF/BEMO, THF/BMMO, and THF/BFMO to various molecular weights ranging from 15,000 to 40,000. Subsequent block linking of these polymers with 20,000 BEMO would reveal the ideal block size.

The physical nature of these copolymers based on monomer ratio was ob- served. We found that generally 50/50 mole ratios of THF:oxetane in the copolymer yielded polymers that were waxy in nature with glass transition

temperatures ranging from -45° to -68°C. When polymers were produced with higher THF contents the melting point was reduced (Ref 1 BAMO/THF). This property will affect the melt viscosity of the final TPE. It can be seen that this portion of the work has many variables and will have a dramatic effect on the final block polymer. Only insertion of the soft block and evaluation of the resultant material will reveal the soft block's final property.

The second part of this task was to synthesize internally plasticized THF polymers. Internally plasticized polymers exhibit the property of appearing already plasticized, i.e., they have low viscosity and low Tg. If we were to synthesize poly (THF) and then plasticize it with one of the many plasticizers available we would expect the polymer/plasticizer mixture to have a low viscosity, and when cured, have good elongation and flexibility. If we were to synthesize a polymer of THF with a modification built in that would result in the polymer exhibiting the same property as the plasticized polymer, we would then consider it to be internally plasticized. This technique is known for some materials, and is obtained by the insertion of long hydrocarbon chains into the backbone of the polymer. It is known that a drop of 50°C in the brittle point of poly (methylmethacrylate) is obtained if a ten carbon side group is inserted through the ester functionality. This material then acts as though already plasticized. The internal plasticization is caused by the long chain hydrocarbon interrupting the chain folding tendency of the polymer and aids in the lubrication of the polymer. If the side group is longer that 12 atoms then it is able itself to chain fold and the effect is lost. With this in mind we synthesized a series of internally plasticized poly (THF) polymers. For this work we copolymerized THF with, in one case OMMO and in another BMEMO. OMMO contains ten atoms that when copolymerized with THF insert a component having a ten atom side chain. BMEMO has a simular side group but contains two ether oxygen atoms in each side group which would add a more flexible nature. This flexibility may have an effect on the viscosity of the final material. In subsequent work on determining the reactivity ratio of OMMO:THF we found that the copolymer is difficult to synthesize by conventional means and this work will be redirected towards the synthesis of internally plasticized oxetane copolymers.

Next we considered the synthesis of the block copolymers. Each block had been presynthesized to various molecular weights. For the initial block

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copolymer we took a series of soft blocks based on the copolymerization of BMMO/THF. This series consisted of various molecular weights (6,000 to 35,000) and monomer ratios, 80:20 THF:BMMO to 50:50 THF:BMMO. These blocks were end capped with 6,000 BEMO end blocks by reaction of the center block with phosgene to form the bischloroformate, then reaction with homo (BEMO). Our initial evaluation of these materials was to melt cast the final polymer in a vacuum oven at 100°C and visually inspect the sample. After a few combinations it was readily apparent that the optimized block size and composition was close to 50:50 BMMO:THF at a block size of 20 to 30,000 with the BEMO block of 6,000. Theoretical calculations completed at this time confirm the experimentally determined block size. A more detailed characterization is being conducted at Lehigh University on a project specifically set up to evaluate these block polymers. A more detailed report will be given by them at a later date.

MOLECULAR WEIGHT DETERMINATION

The molecular weight of polymers synthesized on this program are sufficiently different in structure and molecular weight than molecular weight standards available for calibration that we are constantly concerned about the accuracy in quoting absolute molecular weights. If we use commercially available standards (PPG, PEG, etc.) we must extrapolate outside of the actual range of molecular weights used in the calibration, a dangerous thing to do. Obviously molecular weight fractionation of each individual polymer synthesized for the subsequent calibration of the GPC would be the ideal case, but as we are synthesizing a considerable number of different polymers this would be prohibitive. Therefore, we have evaluated a "middle of the road" technique. We obtained a series of polymer standards, none of which describe our polymer systems, but each of which describe a possible configuration or molecular weight. These polymers are poly (ethylene oxide), poly (tetrahydrofuran), and poly (glycol adipate). The retention times of each polymer system were then graphically presented, and a least squares plot made. The calibration plot thus derived is given in Figure 1 and it is clear that a significant increase in correlation is obtained. As far as GPC determination of molecular weight is concerned we use this calibration curve exclusively.

MOLECULAR WEIGHT (X 10^3)

1,000
500
100
50
10
5
1
0.5
0.1

CALIBRATION STANDARDS

O PTHF
□ PPG
△ PGA

LOGY = 8.285 -0.4118X

S$_{x/y}$ = 0.8471

F = 3927

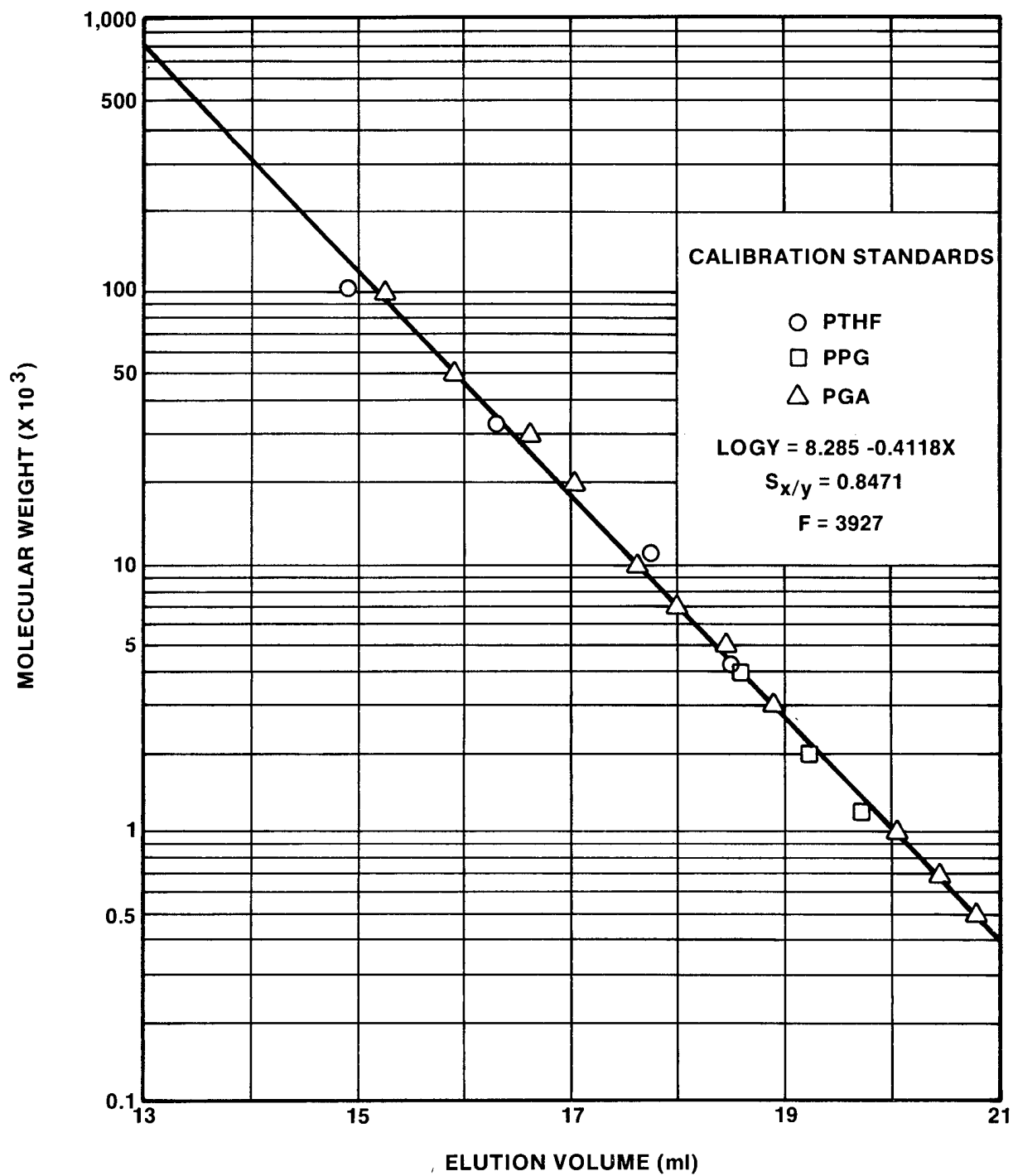13   15   17   19   21

ELUTION VOLUME (ml)

Figure 1. GPC Calibration Curve

POLYMER EVALUATION

Energetic Polymers

For the purpose of this initial evaluation of the nitrate ester polymers we limited the polymer systems to NMMO, BNMO/NMMO, and BAMO/BNMO. The first question to be answered was would the polymers be thermally stable enough for serious consideration. We conducted Taliani and VTS stability studies and compared the results with those obtained from the evaluation of TMETN and NG. The results clearly showed that all three polymer systems were more stable than TMETN and NG, with or without stabilizers. The outgassing from NMMO was found to be 40% lower than TMETN both in the 23 hour Taliani test and in the 48 hour VTS test. BAMO/BNMO outgassing was zero in the Taliani test without stabilizer. DSC analysis of these polymers revealed an onset of exotherm at 468°K, 18°K higher than that recorded for TMETN. We can conclude from these preliminary data that the polymers are at least as stable as nitrate ester plasticizers and warrant a more detailed study.

From these results we prepared gumstocks from the poly (NMMO) prepolymer, NMMO being considered representative of the nitrate ester polymer series. Poly (NMMO) was readily curable at an NCO:OH ratio of 1.5:1. The Shore A hardness was measured at 42. When a plasticized gumstock was prepared using a Pl/Po ratio of 2.3:1 with TMETN, a Shore A hardness of 8 was obtained. Consistent cures were obtained using either DBTDL or TPB as a cure catalyst.

Prior to beginning a full formulation study we ran extensive ingredient compatibility and safety tests. The data clearly showed that the cured and uncured formulations were well within the limits acceptable for nitrate ester based propellants. The impact sensitivity, electrostatic discharge test, and sliding friction test for small hand mix propellants showed a decrease over the sensitivity of the components. The thermal stability at 300°F in the autoignition test was better than that normally obtained from nitrate ester plasticized propellants.

Two small mixes of an NMMO propellant were then prepared to obtain burn rate data. We chose a simple 70 and 75% loaded ballistic type propellant for this work. The samples were cast into plastic straws and subjected to an acoustic burn rate test. The results are given in Figure 2. The 70% solids propellant burned at 0.21 ips at 1,000 psi whereas the 75% solids burned at
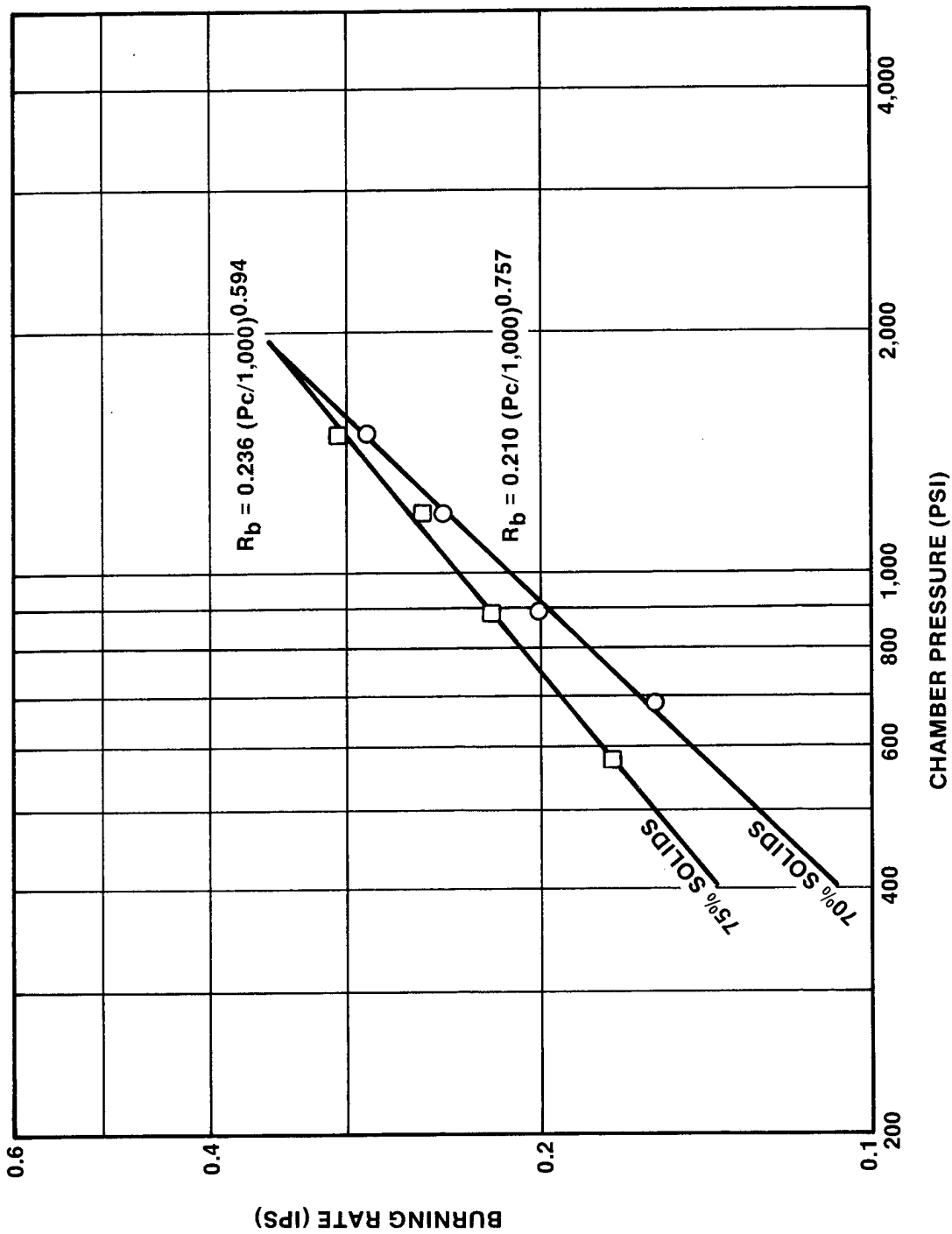
Figure 2. Strand Burning Rate vs Pressure of NMMO Propellants

The axes of the figure read:
- CHAMBER PRESSURE (PSI)
- BURNING RATE (IPS)

Equations shown on the plot:

$$R_b = 0.236 \left(P_c/1{,}000\right)^{0.594}$$

$$R_b = 0.210 \left(P_c/1{,}000\right)^{0.757}$$

Curve labels: 75% SOLIDS, 70% SOLIDS

84589-8B

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0.24 ips at 1,000 psi. The burning rate slopes were 0.76 and 0.59, respectively. This high burning rate slope is typical of the results obtained with other baseline propellants when burned in plastic straws. The overall conclusion drawn from these results is that the NMMO binder has not affected the burn rate of the formulation, only increased the I_{sp} of the formulation.

Further work is in progress to test the burn rate of small scale motors.

Thermoplastic Elastomer Evaluation

Because of a parallel research program being conducted at Lehigh University specifically designed to conduct a more thorough characterization of our thermoplastic elastomers, we have restricted our characterization. The only characterization we have done is a visual observation of polymer cakes and melt cast samples, molecular weight determination, and dynamic modulus tensile measurements.

The material that has shown the greatest potential for a first generation LOVA TPE is that derived from BEMO-BMMO/THF-BEMO. The BEMO blocks were found by GPC to be 6,000 molecular weight and the center block 26,000. The final polymer, after block linking, had a molecular weight of 43,000. The discrepancy is likely due to inaccuracies at these higher molecular weights requiring extrapolation above available standards. The polymer "cake" was easily melt castable at 95°C under vacuum. Obviously a lower melt viscosity was noted if the casting was done at 110°C or higher. The melting point of the TPE was determined to be 86°C.

We determined the melt viscosity to be 280 poise at 95°C. When melt cast and cooled to less than 70°C we found the material to be very tough and elastomeric. The gross glass transition temperature by DSC was found to be -53°C. The Instron tester analysis gave a maximum stress of 603 psi at 35% elongation at which point necking occurred, and final fracture was noted at 600% elongation. This necking is indicative of spherulite formation. A Shore A hardness of 89 was recorded, a value which is in accordance with commercially available TPEs, e.g., Kraton.

Dynamic mechanical properties recorded on the RDS showed extremely good results. The G', G", G*, and tan delta plots are given in Figures 3 thru 6. The results clearly show that mechanical integrity is maintained up to 75°C
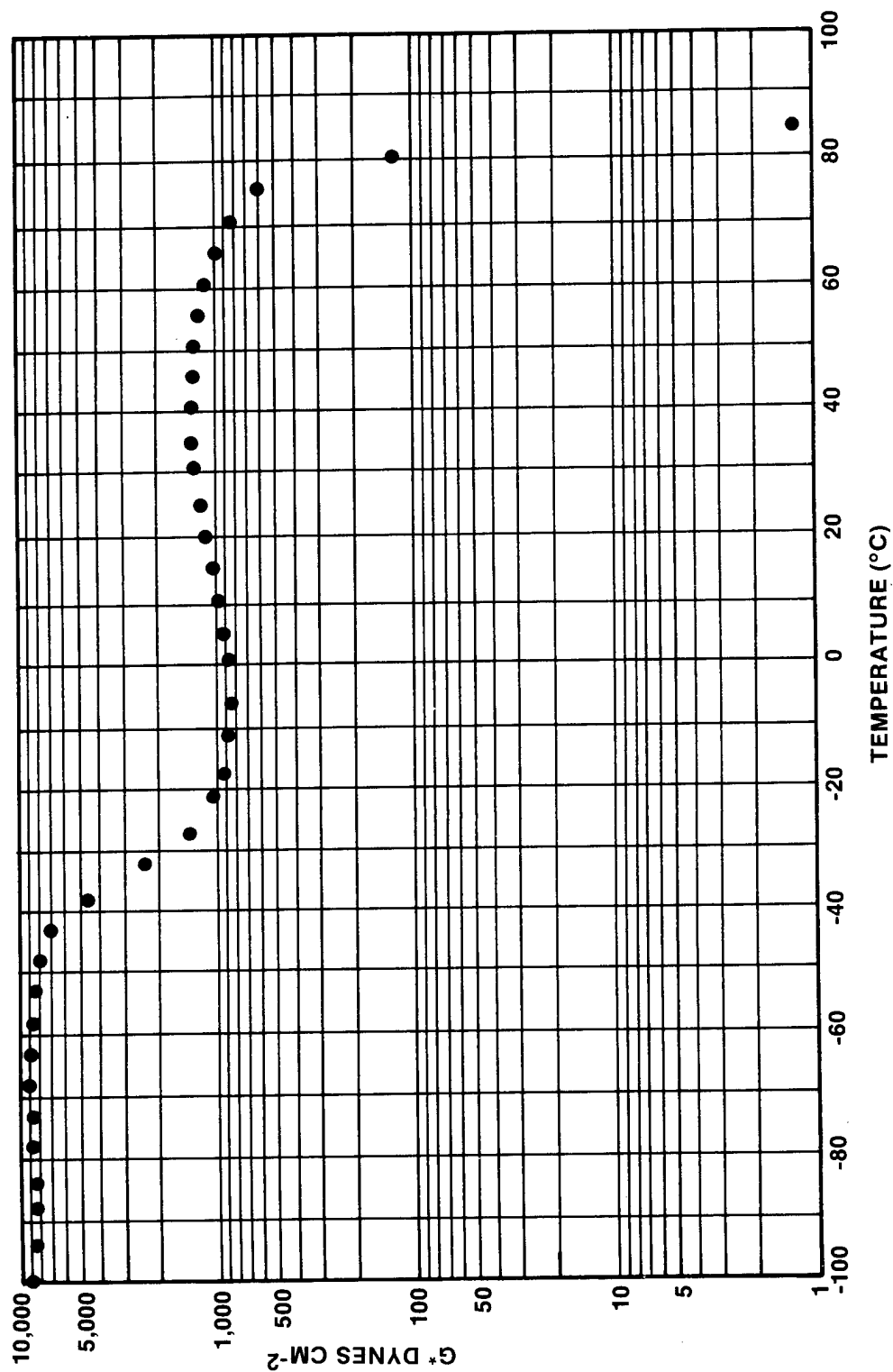
Figure 3. BEMO-BMMO/THF-BEMO Triblock Thermoplastic Elastomer
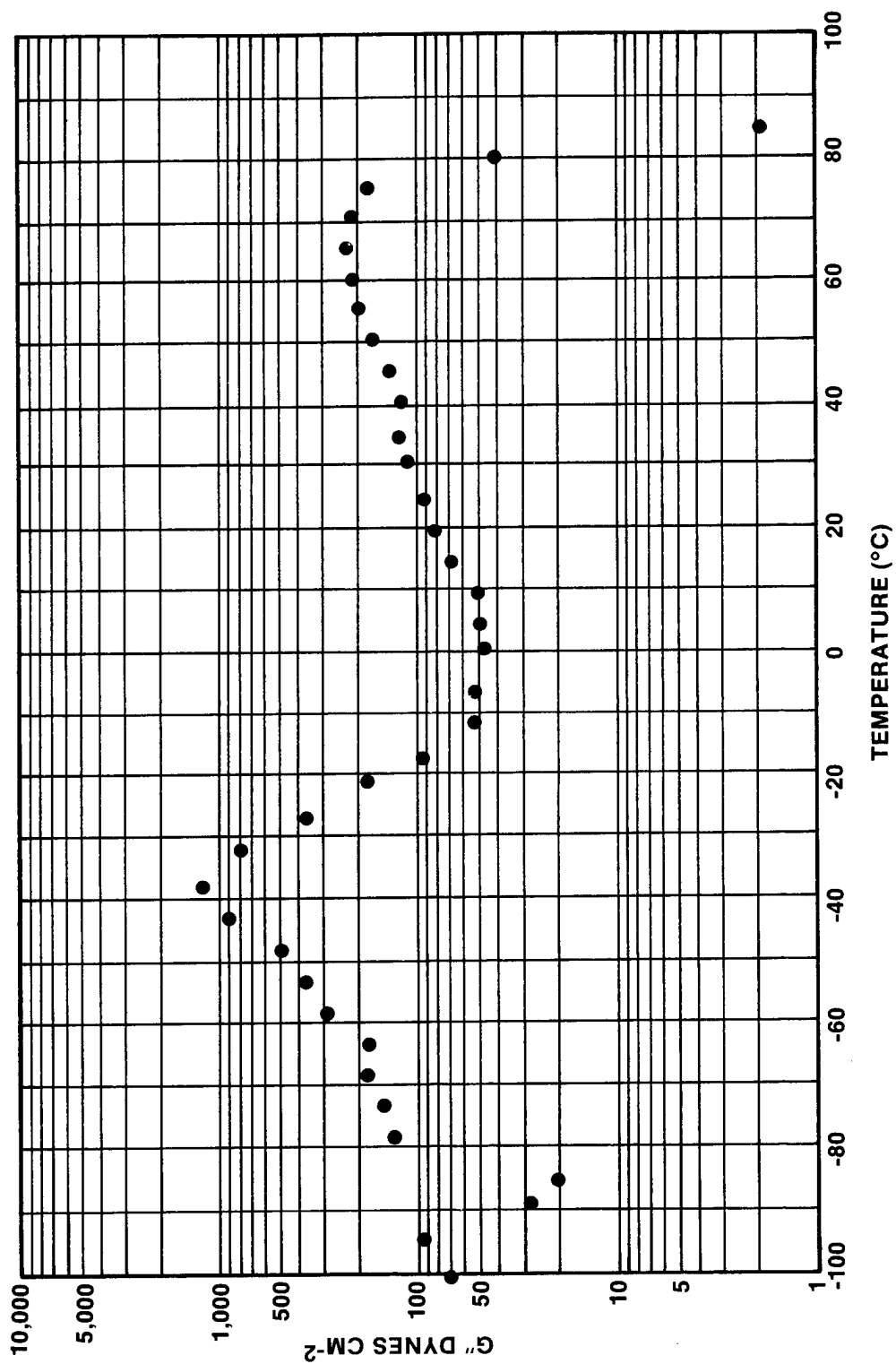
84589-8C

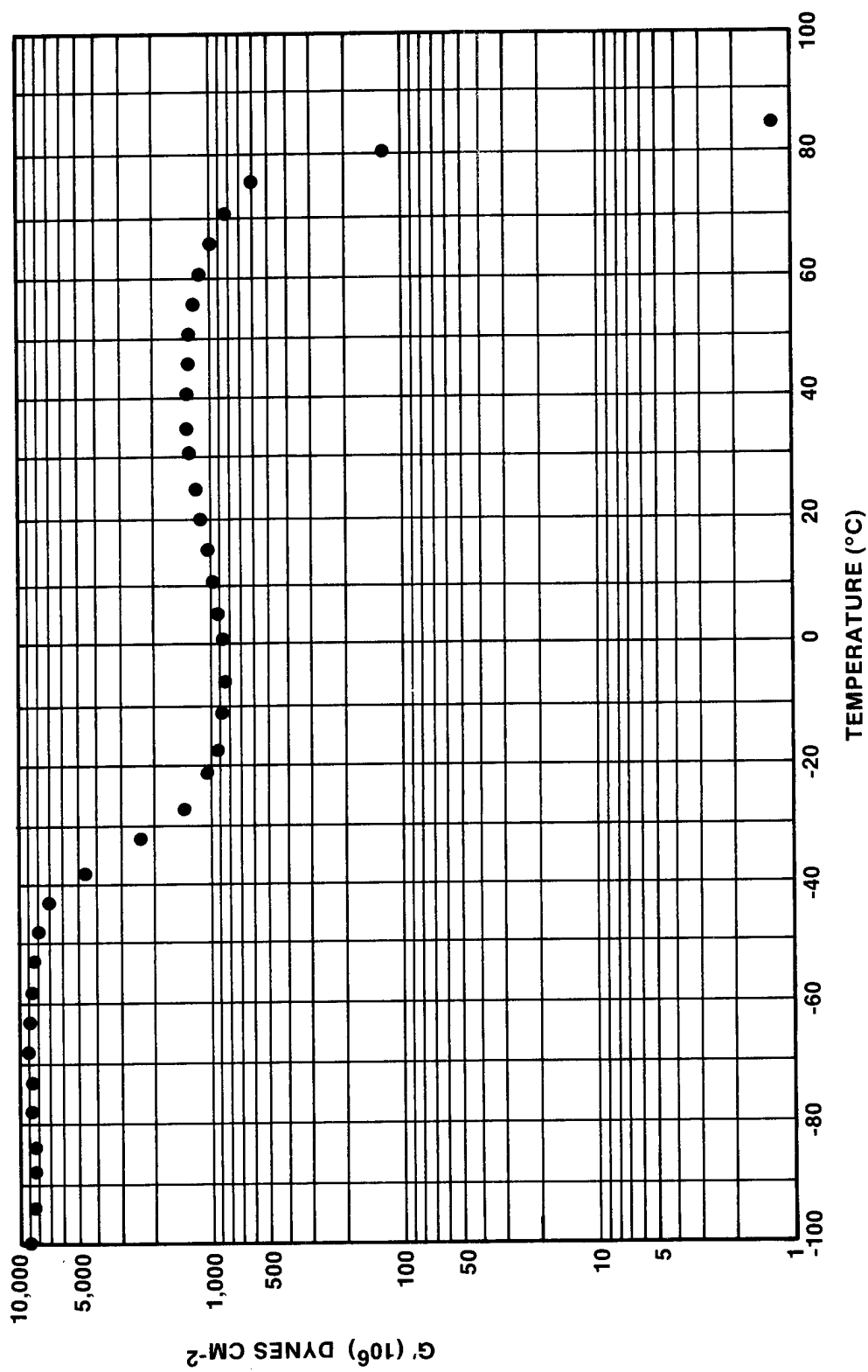Figure 4. BEMO-BMMO/THF-BEMO Triblock Thermoplastic Elastomer

84589-8D

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Figure 5. BEMO-BMMO/THF-BEMO Triblock Thermoplastic Elastomer
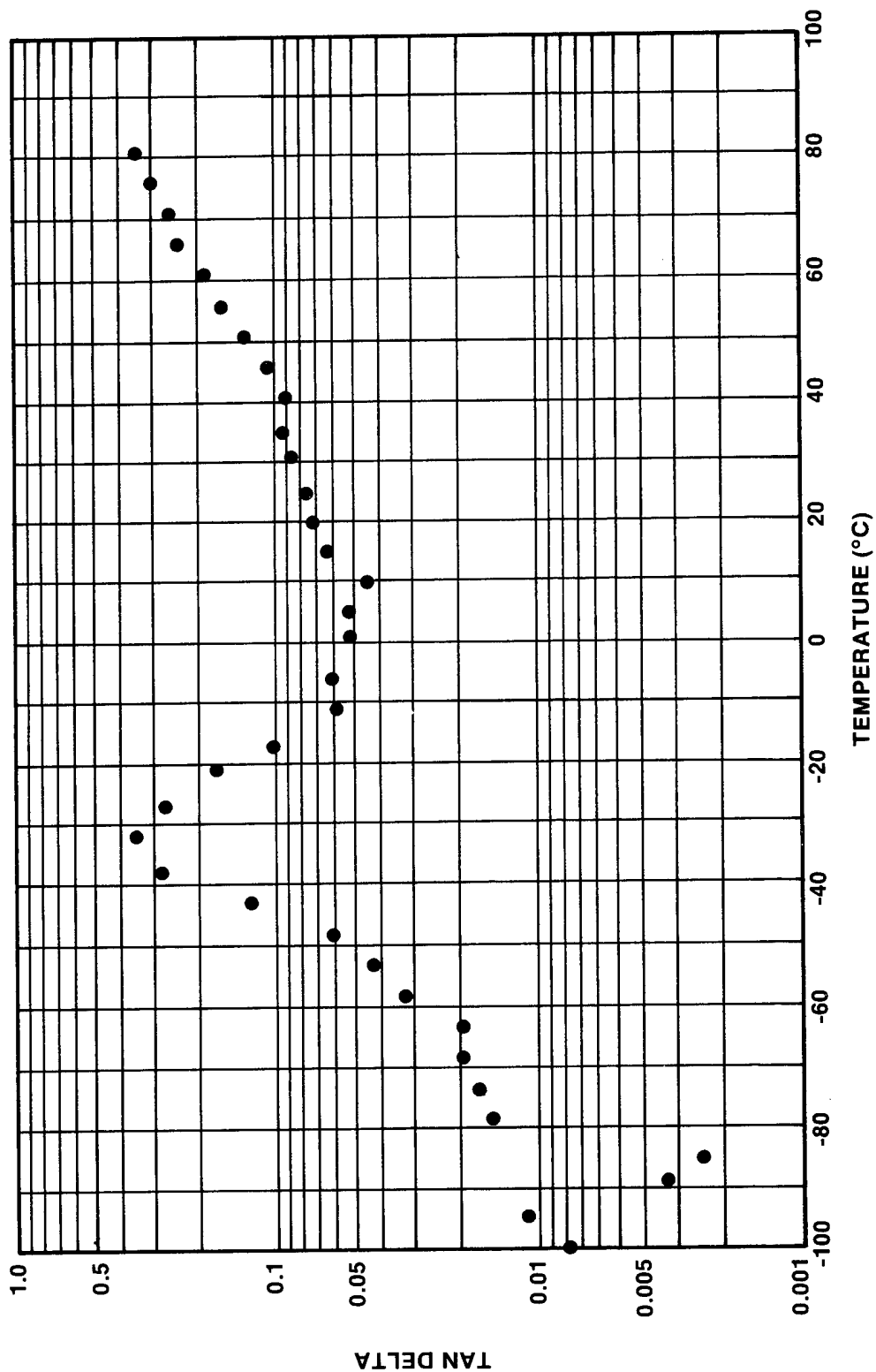
84589-8E

Figure 6. BEMO-BMMO/THF-BEMO Triblock Thermoplastic Elastomer
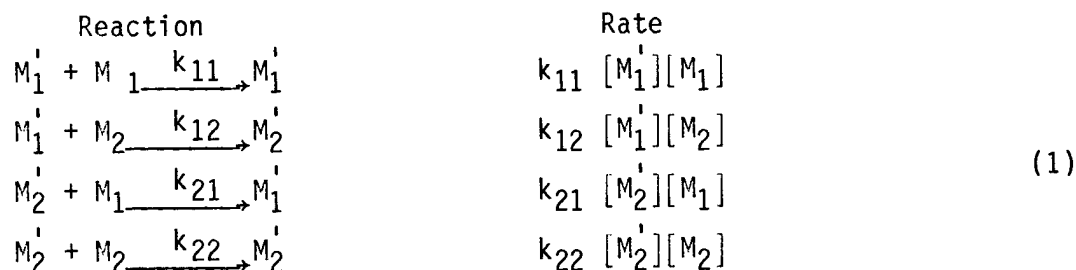
84589-7A

20

at which point all properties are lost over the next 2°C. The material is extremely tough, if not leathery, and fulfills the basic requirements of the program.

<div align="center">KINETICS STUDY</div>

1. Reactivity Ratios

During our previous work we relied on matched monomer pairs to produce liquid prepolymers. We reported a series of reactivity ratios and demonstrated that if monomers were chosen with simular reactivity then a random copolymer, i.e., ideal copolymer, would result. If the reactivity was not matched, then a block, or mixture of homo polymers would result and the properties would not meet our requirement. As our work has progressed we have further developed the technique of measuring reactivity ratios and used this information extensively in the production of both energetic and nonenergetic polymers.

The method we used to determine the reactivity ratio of monomer pairs is based on the published work of Alfrey (Ref 5), Mayo (Ref 6), Simha (Ref 7), and Wall (Ref 8). This method is based on the assumption that the rate of addition of monomers to the growing end of a "living polymer" depends only on the nature (reactivity) of the end groups of the growing chain. There are four possible pathways in which monomers can add:

$$
\begin{array}{cc}
\text{Reaction} & \text{Rate} \\
M_1' + M_1 \xrightarrow{k_{11}} M_1' & k_{11}\,[M_1'][M_1] \\
M_1' + M_2 \xrightarrow{k_{12}} M_2' & k_{12}\,[M_1'][M_2] \\
M_2' + M_1 \xrightarrow{k_{21}} M_1' & k_{21}\,[M_2'][M_1] \\
M_2' + M_2 \xrightarrow{k_{22}} M_2' & k_{22}\,[M_2'][M_2]
\end{array}
\tag{1}
$$

where M_1 and M_2 are the monomers and M_1' and M_2' are the growing ends. An assumption that must be made is that the concentration of M_1' and M_2' remain constant. This requires that the rate of conversion of M_1' to M_2' must equal the rate of conversion of M_2' to M_1'. Thus:

$$
k_{21}[M_2'][M_1] = k_{12}[M_1'][M_2]
\tag{2}
$$

The rates of disappearance of the two monomers are given by:

$$\frac{-d[M_1]}{dt} = k_{11} [M_1'] [M_1] + k_{21}[M_2'] [M_1]$$

$$\frac{-d[M_2]}{dt} = k_{12} [M_1'] [M_2] + k_{22}[M_2'] [M_2]$$

(3)

The reactivity ratio of each monomer is defined as:

$$R_1 = k_{11}/k_{12}$$
$$R_2 = k_{22}/k_{21}$$

(4)

By combining equations (2) and (3) it is shown that the composition of the copolymer formed at any instant is given by the copolymer equation:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{R_1 [M_1] + [M_2]}{R_2 [M_2] + [M_1]}$$

(5)

Thus the reactivity ratio is defined as the ratio of the rate constants for a given "living copolymer."

Since the rate constants for initiation and termination do not appear in the copolymer equation, the polymerization is independent of the overall reaction rate and initiator concentration. Also, in most cases, it is independent of inhibitors, chain transfer agents, and solvents. If, however, there is a change in polymerization mechanism during the polymerization, then the theory does not hold true.

There are a number of known types of copolymerization. If the propensity of two monomers towards polymerization are the same, i.e., their reactivity ratios are close, then an ideal copolymer will result. In this case $k_{11}/k_{12} = k_{21}/k_{22}$, or $R_1 = 1/R_2$, the distribution of each monomer in the chain will be random, and its concentration will only depend on the comonomer concentration in the monomer feed. In this case the copolymer equation (5) reduces to:

$$\frac{d[M_1]}{d[M_2]} = R_1 \frac{[M_1]}{[M_2]}$$

(6)

In the case where $R_1 = R_2 = 0$, each monomer prefers to react with the other monomer. In this case an alternating copolymer will result, and will be totally independent of the feed stock composition. The copolymer equation (5) reduces to:

$$\frac{d[M_1]}{d[M_2]} = 1 \tag{7}$$

When R_1 and R_2 are both > 1 then M_1' and M_2' prefer to react with their own

monomer and, depending on the values of R_1 and R_2 either a block copoly-

mer, a mixture of homopolymers, or polymerization of only one monomer may

result.

The determination of the reactivity ratio of a monomer pair requires the

solution of the copolymer equation (5) for R_1 and R_2. The method chosen

in our work is a graphical method developed by Kelen and Tudos (ref 9) which

is based on the prior work of Fineman and Ross (ref 10).

By this method we define x and y as:

$$\frac{[M_1]}{[M_2]} = x \tag{8}$$

$$d[M_1]/d[M_2] = y$$

we can write equation (5) as:

$$y = x \frac{R_1 x + 1}{R_2 + x} \tag{9}$$

Fineman linearized equation (9) as:

$$G = R_1 F - R_2 \quad \text{and/or} \quad \frac{G}{F} = -R_2 \frac{1}{F} + R_1 \tag{10}$$

where the transformed variables are:

$$G = \frac{x(y-1)}{y} \quad \text{and} \quad F = \frac{x^2}{y} \tag{11}$$

In order to overcome some of the disadvantages inherent in the Fineman and

Ross method, Kelen and Tudos (ref 11) introduced the following graphically

envaluable linear equation:

$$\frac{G}{\alpha + F} = \left(R_1 + \frac{R_2}{\alpha}\right)\frac{F}{\alpha + F} - \frac{R_2}{\alpha} \tag{12}$$

where alpha denotes an arbitrary constant, alpha > 0.

Defining two more variables Eta and Xi:

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F} \tag{13}$$

equation (12) becomes:

$$\eta = R_1 \xi - \frac{R_2}{\alpha}(1-\xi) \tag{14}$$

Xi can only take a positive value in the interval (0, 1) and plotting the Eta values calculated from the experimental data in the function of Xi, we obtain a straight line, which extrapolated to Xi = 0 and Xi = 1 gives $-R_2/alpha$ and R_1 (both as intercepts). Alpha serves to distribute the data uniformly in the interval (0, 1) and is chosen as:

$$\alpha = \sqrt{F_M \; F_m} \qquad (15)$$

where F_M is the highest value for F and F_m is the lowest value of F from the data.

In the determination of the x and y, equations (8) are only strictly true under experimental conditions at monomer conversions of near zero. A further refinement by Kelen and Tudos (ref 11) to correct for conversion up to 60% under experimental conditions has been incorporated into the actual determination of R_1 and R_2 in this report.

Experimental Determination of Reactivity Ratios

A jacketed, three neck 15 ml reactor is prepared by cleaning in a sulfuric acid bath. The reactor is carefully rinsed in distilled water and dried at 140°C. A syringe septum is fitted to one of the openings and the flask is flushed with dried nitrogen. A weighed sample of monomers, solvent, and diol initiator is added to the reactor and stirred by use of a magnetic stirrer. When the flask has equilibrated to the desired temperature a weighed amount of boron trifluoride etherate is added and the polymerization allowed to proceed. At the time when sufficient conversion has been achieved (15 to 50%) a syringe is used to withdraw a sample (1 ml), which is placed into a previously weighed 2 ml volumetric flask. The weight of this sample is recorded. To this flask is then added a weighed amount of internal standard (nonane, toluene etc.) and then the contents of the flask are made up to the mark with water wet methylene chloride. This quenches the polymerization. The amount of monomers remaining in the polymerization sample is determined by GC analysis. A detailed account of this procedure is given in Appendix II. We use a Hewlett Packard 5700 gas chromatograph connected to a Hewlett Packard 2290 A integrater. The column is a 1/4 in. by 8 ft 10% OV 101 on chrome Q glass column. The data from the GC along with the weights of the monomers, internal standard, diol, catalyst, and solvent used in the polymerization are then transcribed into a Hewlett Packard 9825 B computer. By the use of the program, see Appendix III, we obtain an instantaneous

polymerization curve, Eta versus Xi plot and the reactivity ratio. The Eta/ Xi plot is used to gage if any points are obviously in error and the instantaneous polymerization plot gives a pictorial assessment of the suitability of the monomer pair to copolymerize.

By this method we have determined the following reactivity ratios:

TABLE I

Monomer Pair	R_1	R_2
BAMO/AMMO	0.92 ± 0.15	1.18 ± 0.24
NMMO/AMMO	0.35 ± 0.10	2.73 ± 0.24
NMMO/BAMO	1.63 ± 0.92	2.55 ± 0.72
OMMO/THF	21.69 ± 0.28	0.05 ± 0.10
OMMO/BMMO	1.23 ± 0.28	0.74 ± 0.11

These results are added to the ones already reported by us (ref 1). The instantaneous polymerization curves and Eta versus Xi plots are given in Figures 7 thru 16.

Further monomer ratios are under study and will be reported when the work is completed.

Most of the monomer pairs that we proposed to use in the various synthesis steps appear to be suitable for their intended use except OMMO/THF. The reactivity ratio of this monomer pair suggests that copolymerization will not be viable and if we attempt to prepare this copolymer we would only obtain a homopolymer of OMMO. Therefore we have not pursued this monomer pair and in fact selected OMMO/BMMO for an internally plasticized soft block for the thermoplastic elastomers.

2. Thermal Decomposition of Poly (BEMO)

To aid in the thermal depolymerization studies being carried out by Lehigh University on the polyether thermoplastic elastomers we undertook a parallel study. The Differential Scanning Calorimetry (DSC) curves obtained from Lehigh University on poly (BEMO) were reported at different heating rates and clearly showed that depolymerization/decomposition was occurring. The reported decomposition was a broad endotherm which was found to be dependent on the rate of heating. For confirmation of these results we undertook a parallel Thermo Gravimetric Analyzer (TGA) analysis. A Gravitronic III TGA made by Theta Instruments was used for this work. The TGA curves for
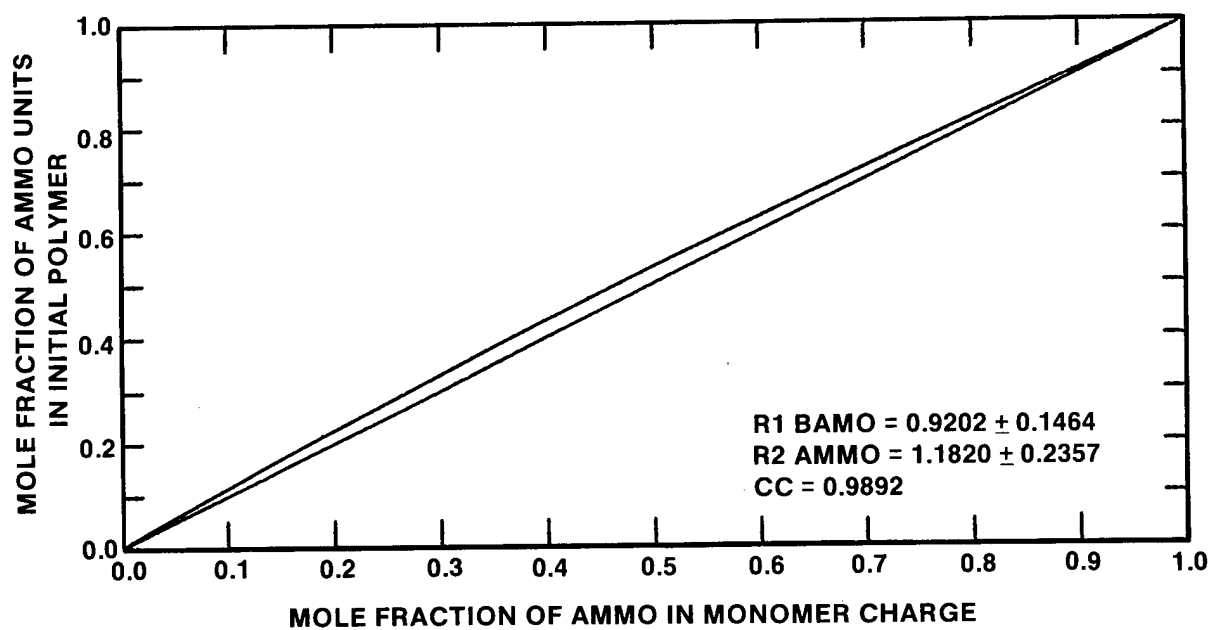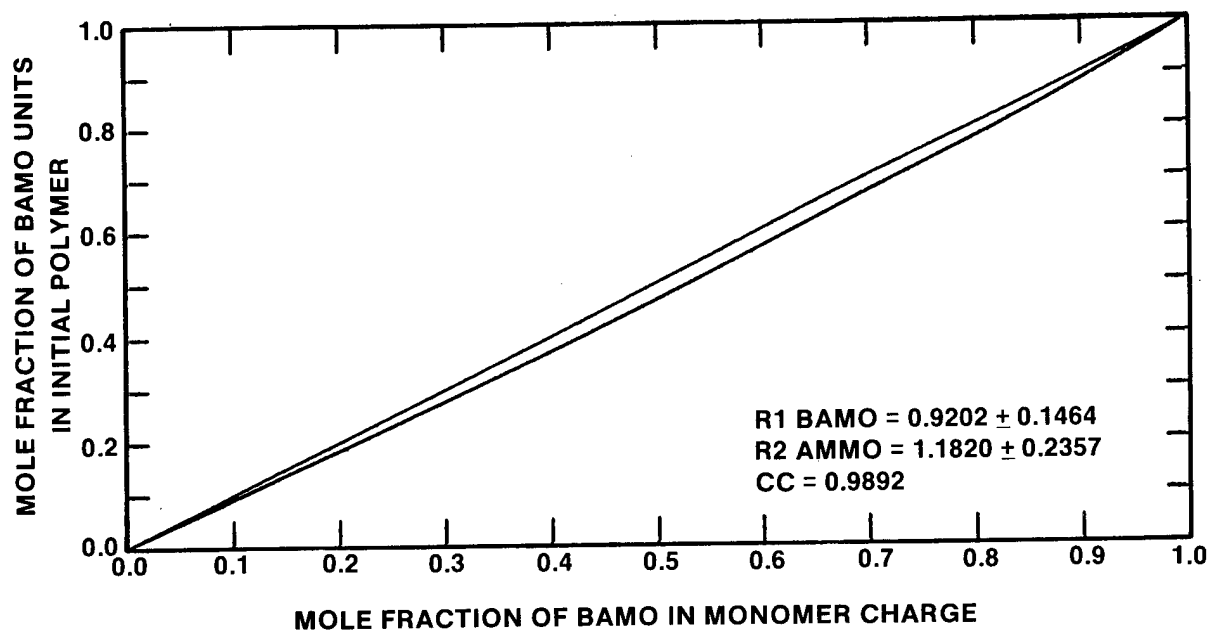
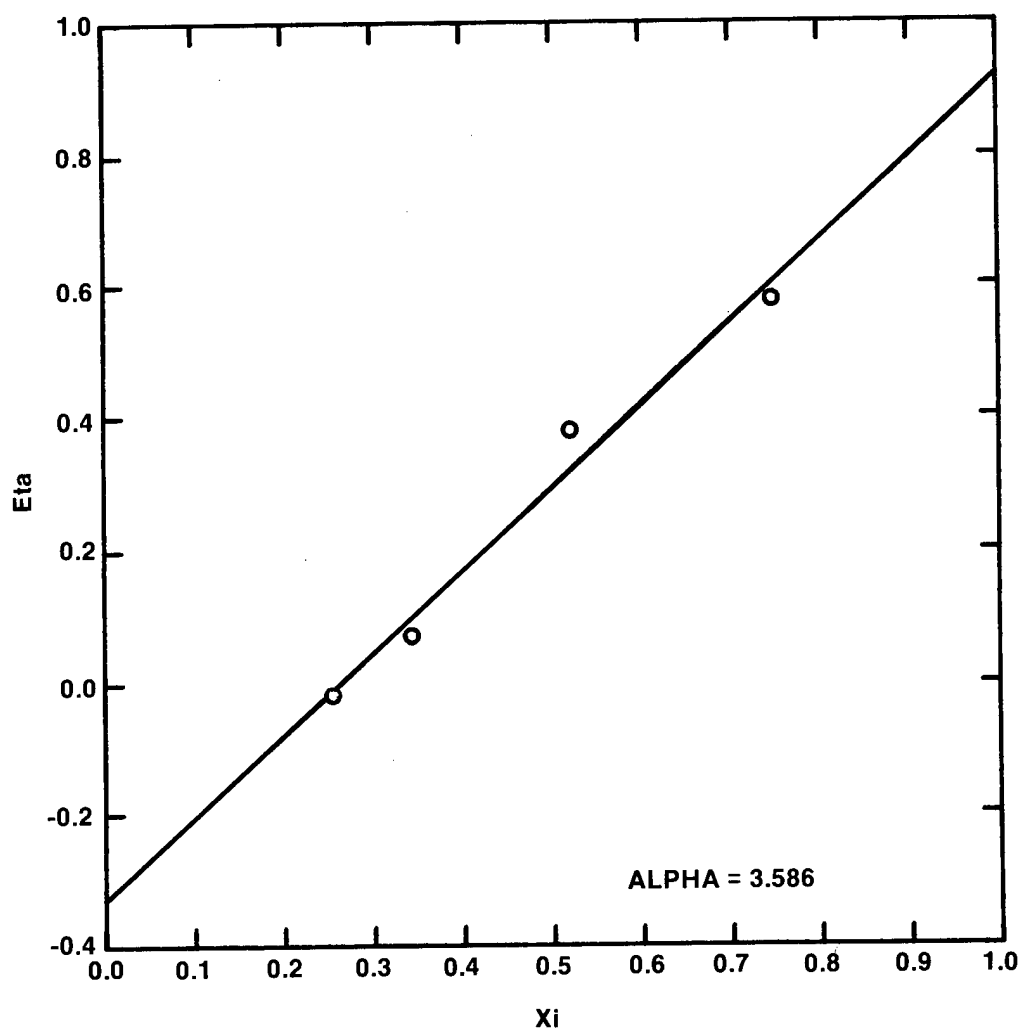Figure 7. Instantaneous Composition Curve of BAMO/AMMO Copolymer
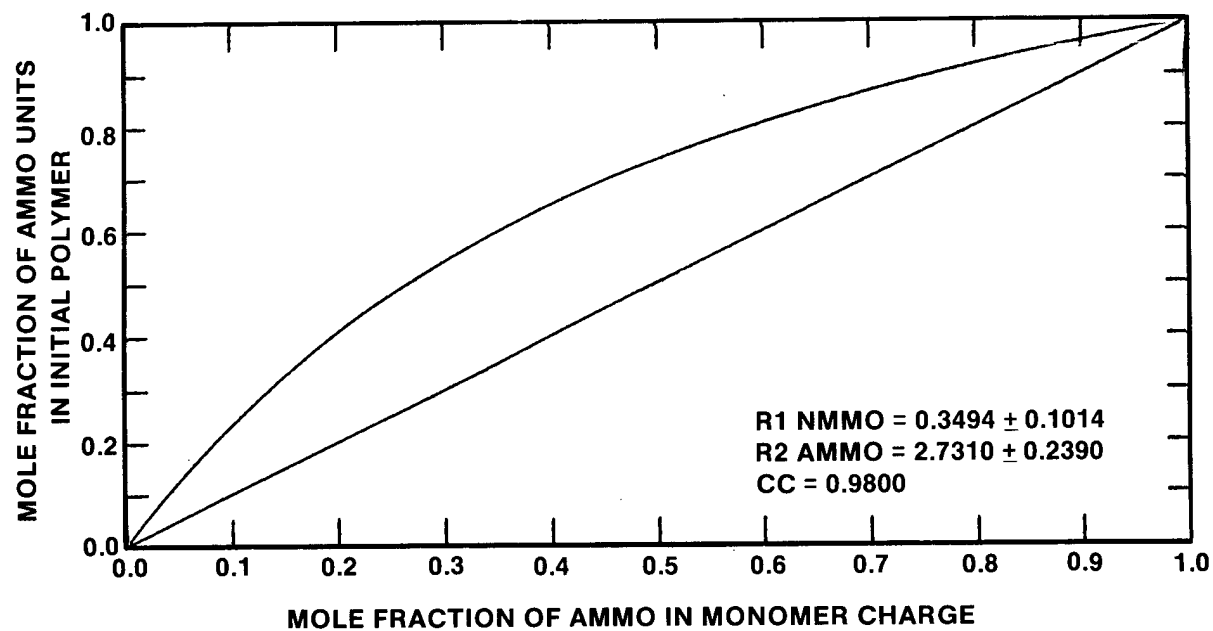
84589-7B
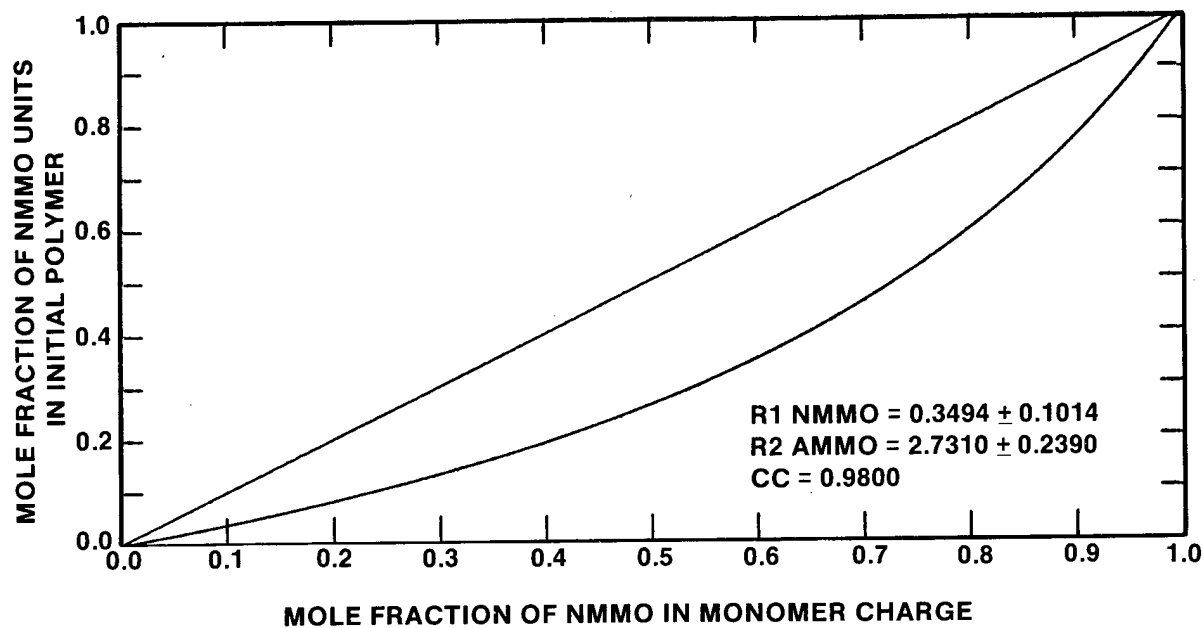
Figure 8. Eta vs Xi Plot for BAMO/AMMO

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R1 NMMO = 0.3494 ± 0.1014
R2 AMMO = 2.7310 ± 0.2390
CC = 0.9800

MOLE FRACTION OF NMMO IN MONOMER CHARGE

R1 NMMO = 0.3494 ± 0.1014
R2 AMMO = 2.7310 ± 0.2390
CC = 0.9800

MOLE FRACTION OF AMMO IN MONOMER CHARGE

Figure 9. Instantaneous Composition Curve of NMMO/AMMO Copolymer

28

R1 NMMO = 1.6279 ± 0.9232
R2 BAMO = 2.5490 ± 0.7246
CC = 0.8912

MOLE FRACTION OF NMMO IN MONOMER CHARGE

R1 NMMO = 1.6279 ± 0.9232
R2 BAMO = 2.5490 ± 0.7246
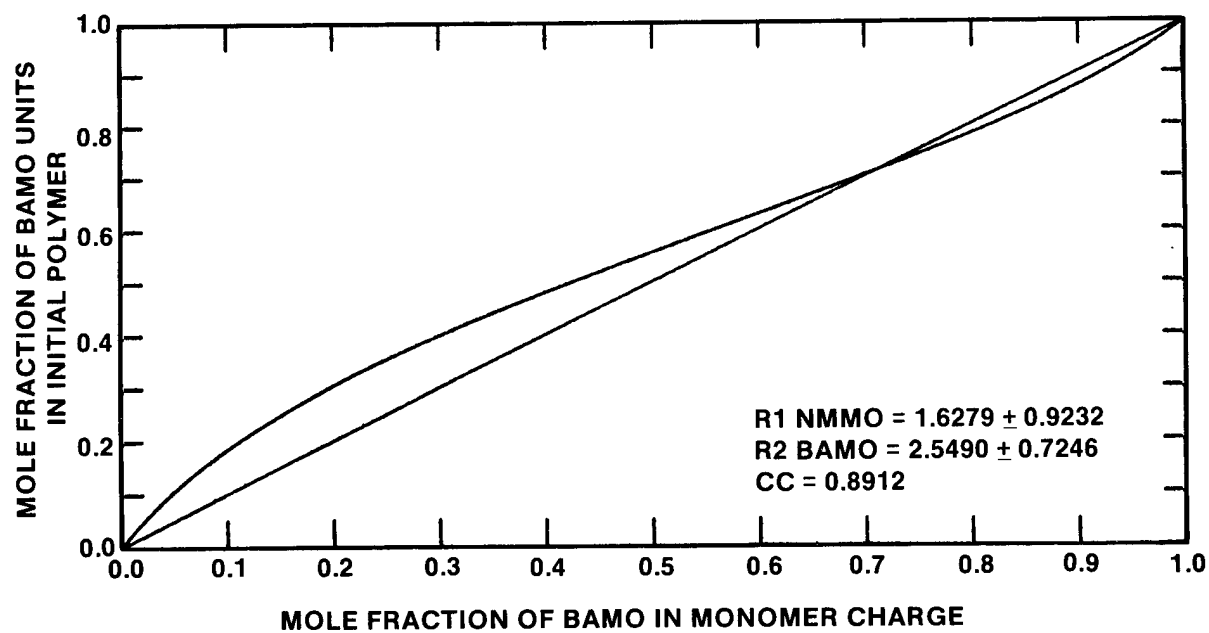CC = 0.8912

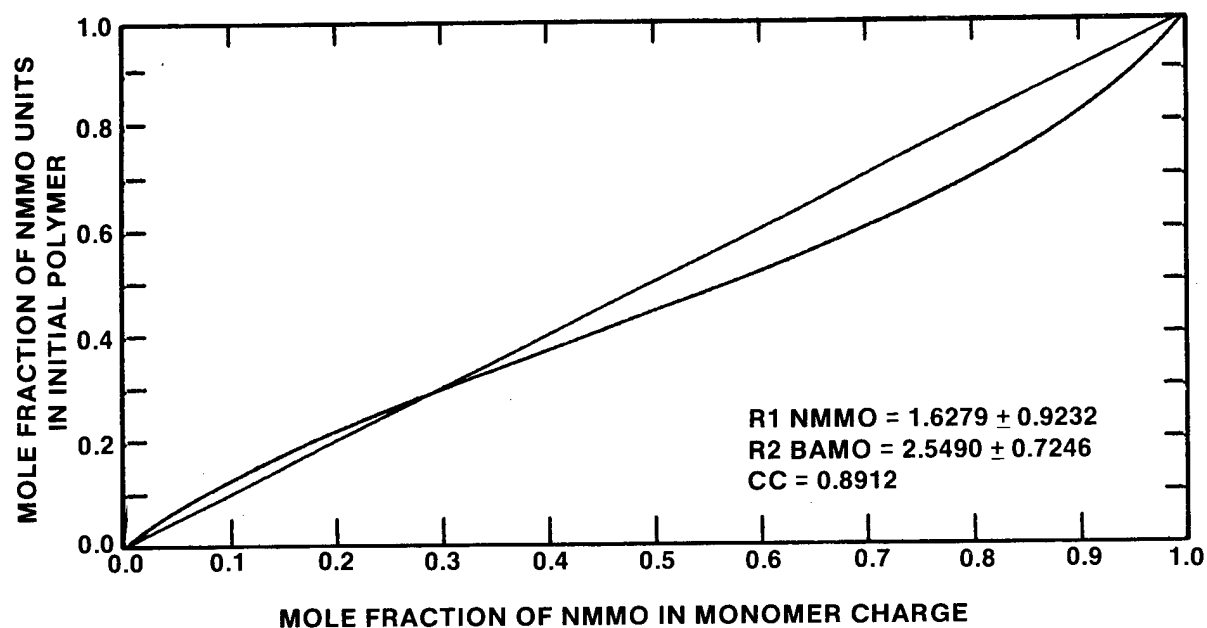MOLE FRACTION OF BAMO IN MONOMER CHARGE

Figure 11. Instantaneous Composition Curve of NMMO/BAMO Copolymer

84589-7F
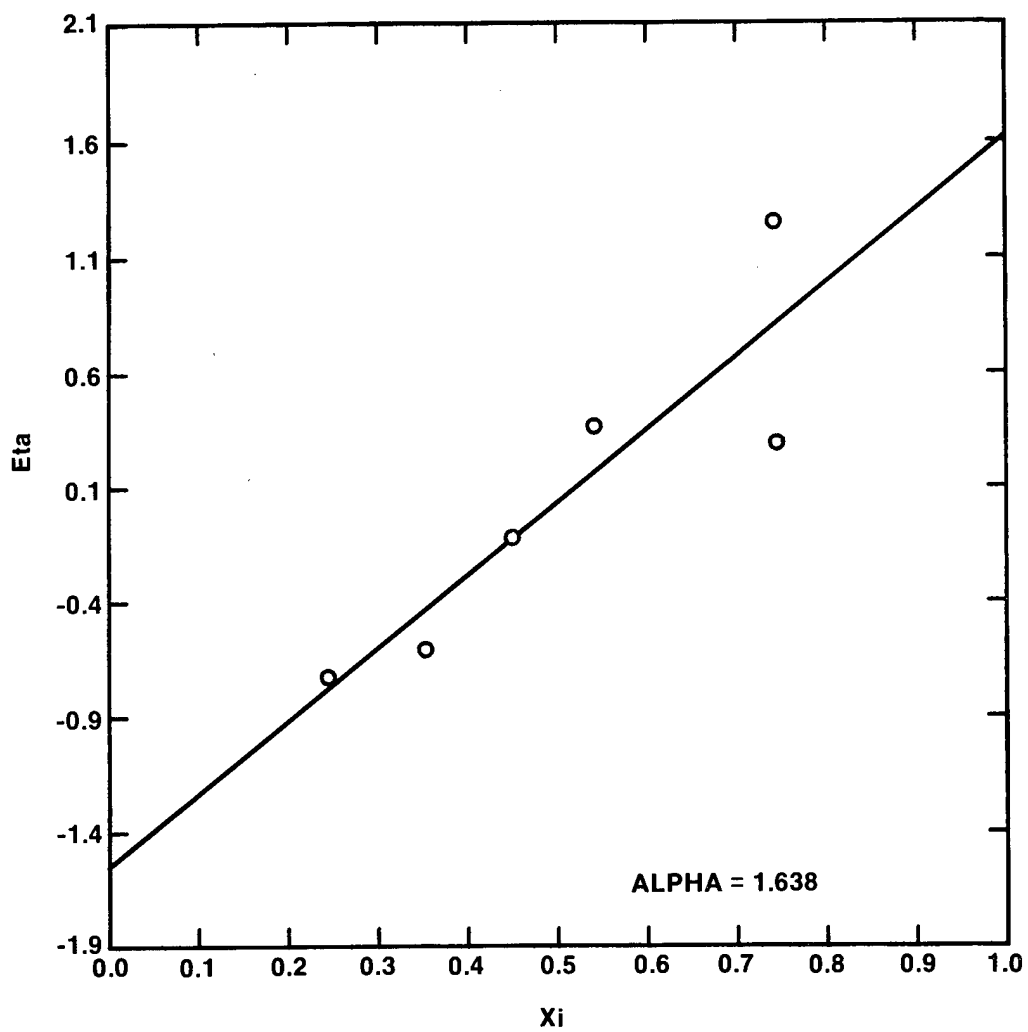
Figure 12. Eta vs Xi Plot for NMMO/BAMO

31

R1 OMMO = 21.6917 ± 9.9936
R2 THF = 0.0516 ± 0.1043
CC = 0.8895

MOLE FRACTION OF OMMO IN MONOMER CHARGE

R1 OMMO = 21.6917 ± 9.9936
R2 THF = 0.0516 ± 0.1043
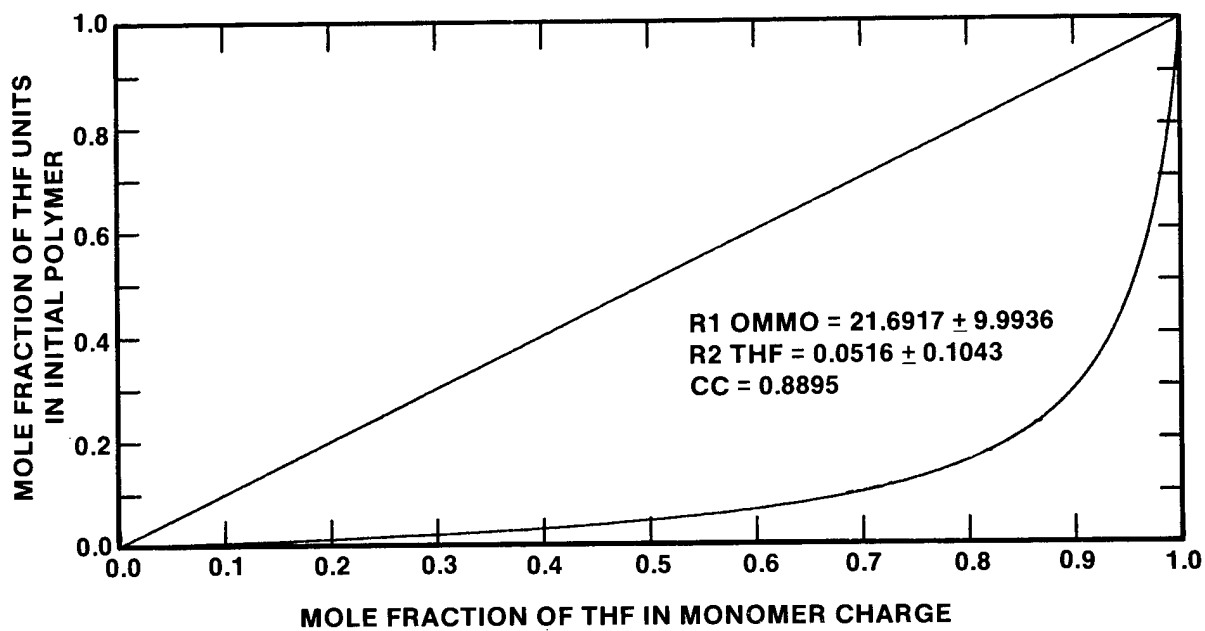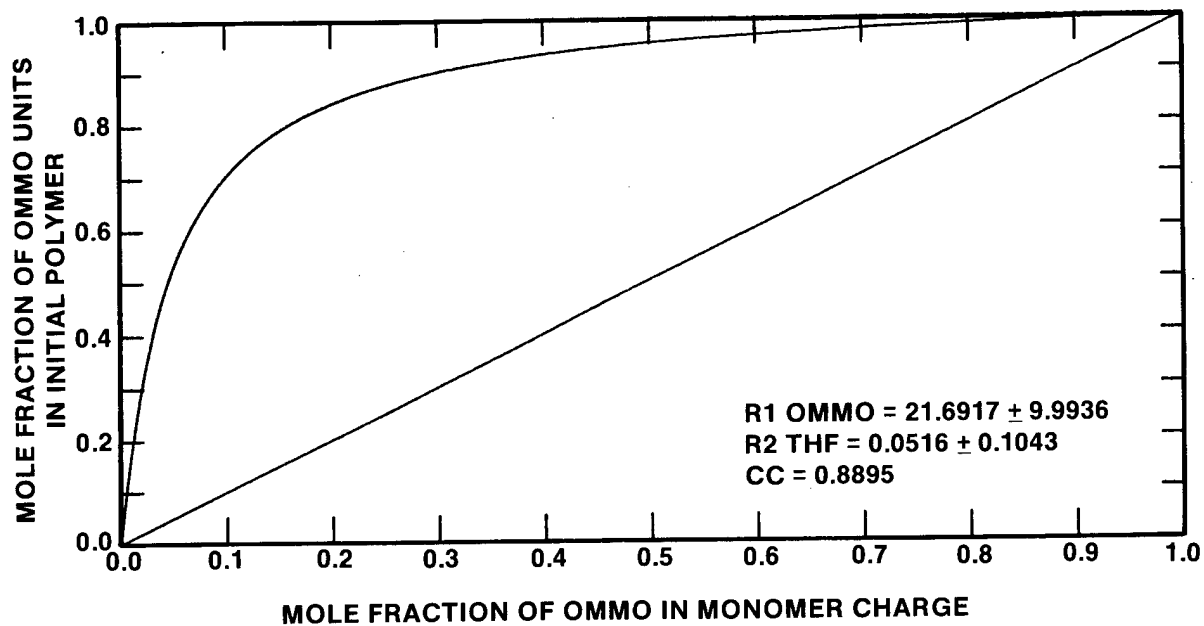CC = 0.8895

MOLE FRACTION OF THF IN MONOMER CHARGE

Figure 13. Instantaneous Composition Curve of OMMO/THF Copolymer

32
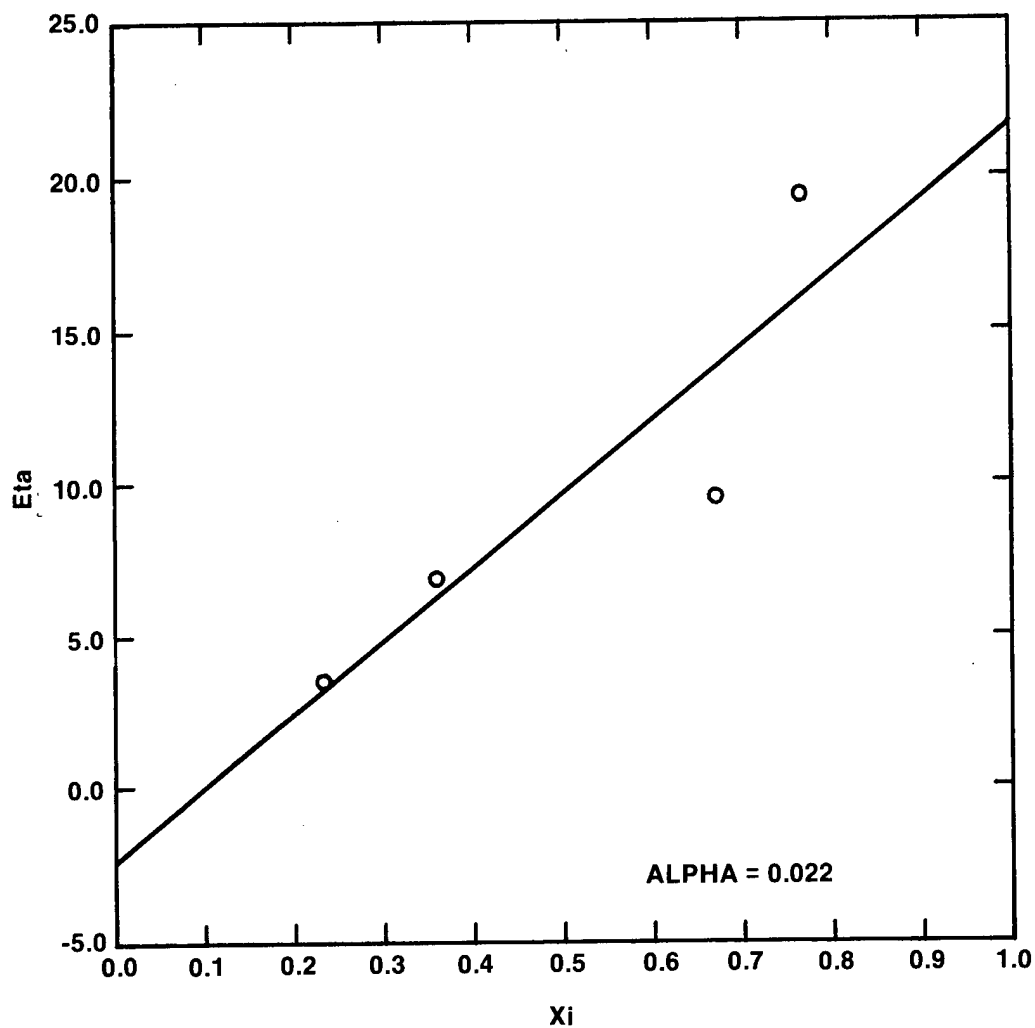
Figure 14. Eta vs Xi Plot for OMMO/THF

33

R1 OMMO = 1.2342 ± 0.2766
R2 BMMO = 0.7429 ± 0.1107
CC = 0.9737

R1 OMMO = 1.2342 ± 0.2766
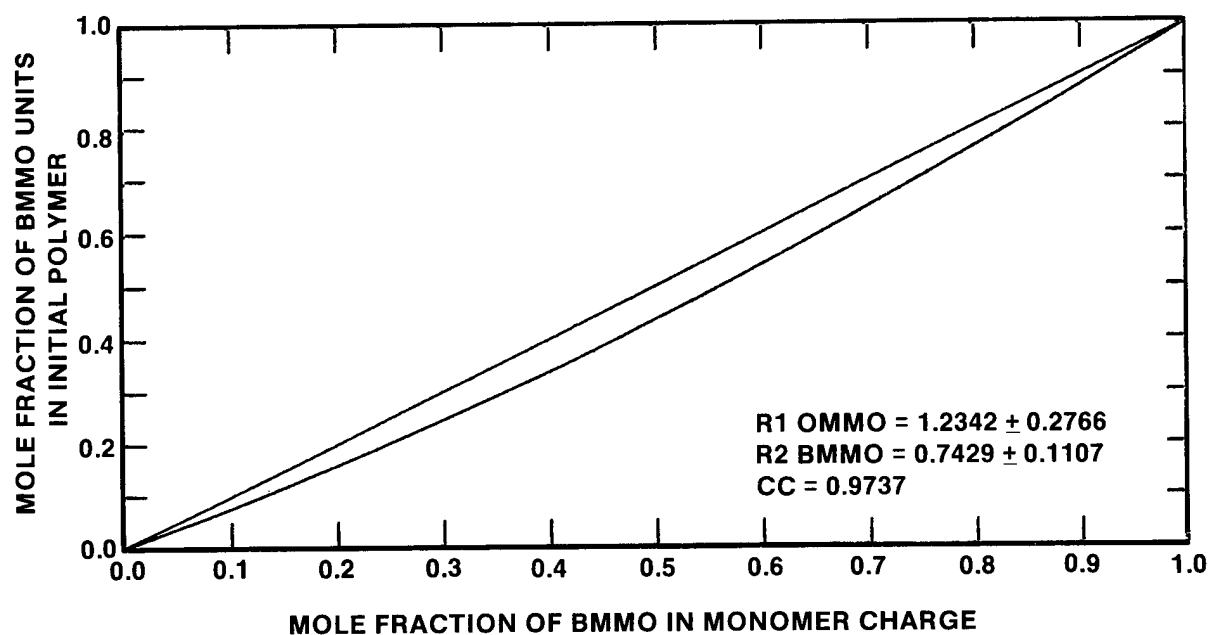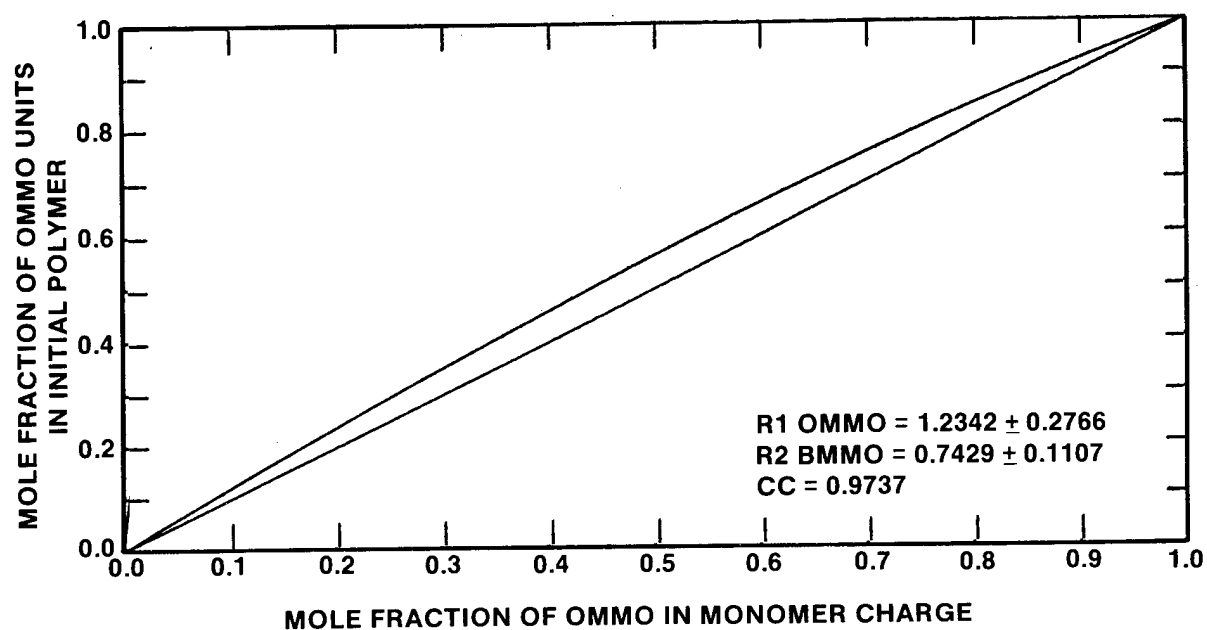R2 BMMO = 0.7429 ± 0.1107
CC = 0.9737

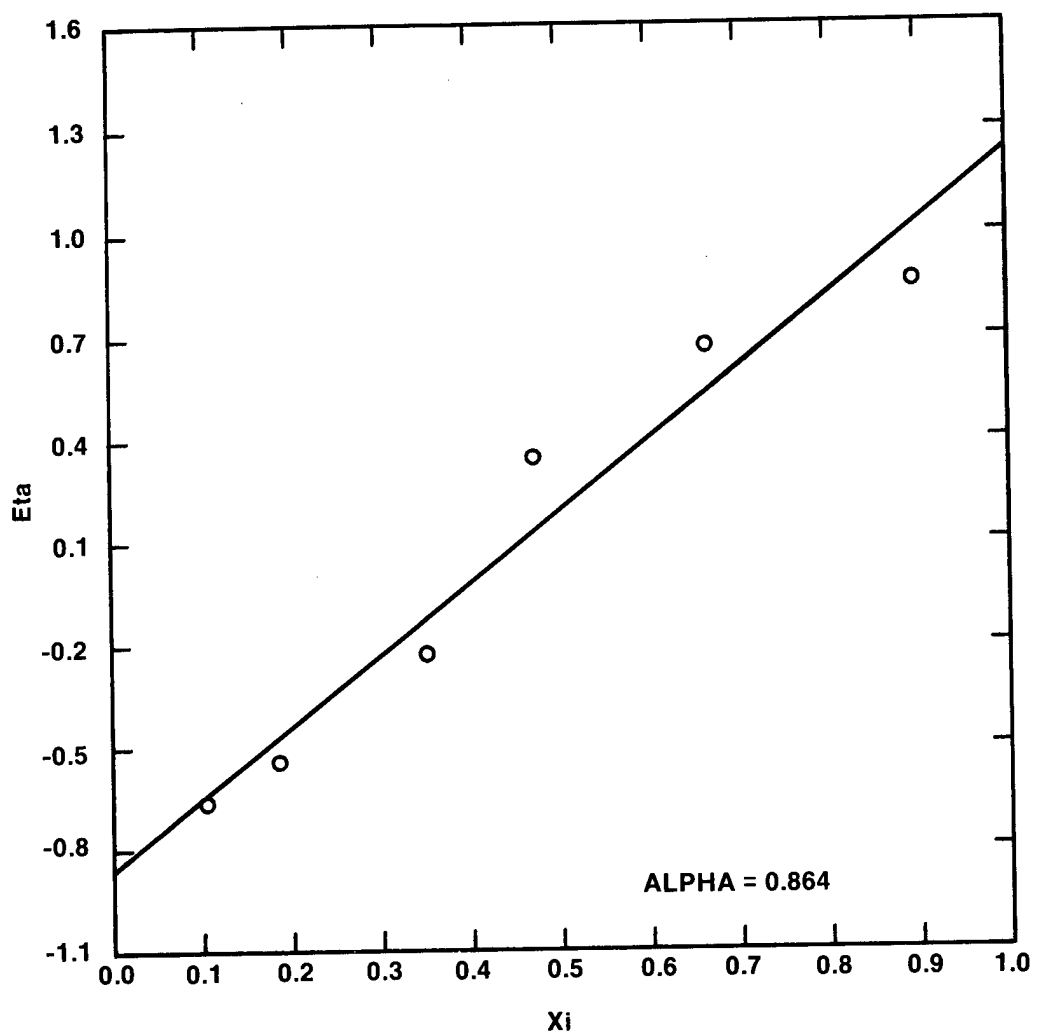Figure 15. Instantaneous Composition Curve of OMMO/BMMO Copolymer

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Figure 16. Eta vs Xi Plot for OMMO/BMMO

35

poly (BEMO) were found to be very complex, and by the shape of the curves, are thought to indicate at least two reactions. The multiple weight loss was not separated enough to obtain an initial temperature for the second reaction; however, if both ethoxymethyl fragments were lost, the mass loss would correlate with the transition region between the two observed reactions in the TGA. The initial temperatures are given in Table II:

TABLE II

Heating Rate °C/min	Atmosphere	Initial Temperature °C
0.5	Air	173
0.5	Nitrogen	182
2	Air	167
2	Nitrogen	164
5	Air	181
5	Nitrogen	210
10	Air	176
10	Nitrogen	220

One isothermal weight change determination was made at each of the following temperatures: 125°, 150°, 175°, 200°, and 225°C. The results obtained indicate a very complex reaction. The lower three temperatures gave zero order kinetics with multiple changes in slope. The higher temperatures indicate higher order reactions.

The initial weight loss for the isothermal traces is proposed to be the loss of entrained solvent and the sample heating up from ambient to set temperature. Although the 125°C has a change in slope, it is small enough that the reaction was assumed to be zero order with a rate constant of 3.3μg/min. The rate constants of 11.2μg/min and 25μg/min were obtained for the second and third reactions on the 150°C isothermal trace. Similarly, for the 175°C isotherm, the rate constants were found to be 41μg/min and 33.4μg/min. The reaction at 200°C gave a straight line with a correlation coefficient of 0.9958 for a second order reaction. The rate constant was found to be 2.12 g^{-1} min^{-1}. The reaction at 225°C also gave a straight line with a correlation coefficient of 0.9997 for a first order reaction with a rate constant of 0.0107 min^{-1}. These results are consistent for a complex decomposition which includes loss of ethoxymethyl groups prior to backbone fracture.

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III. CONCLUSIONS

We have demonstrated that both energetic and nonenergetic polyether polymers can be synthesized that fulfill the objectives for navy applications. We have synthesized two series of energetic polyether glycols that increase the ballistic performance of propellants and show thermal and chemical stability required for application. These polymers are:

1. Azido polyether glycols
2. Nitrate ester polyether glycols

These polymers can improve propellant performance, depending on the application, from 3 to 8 sec I_{sp}. They are fully compatible with co-ingredients, and are thermally stable enough for most applications. Initial formulations and testing have been concluded.

We have synthesized the first of a series of block copolymers based on crystalline and amorphous segmented polymers that can be processed at 85° to 90°C. These polymers, when melt cast, can yield materials that physically range from leathery to soft depending on the size of the individual blocks and the stoiciometry of the blocks to one another. These polymers exhibit endothermic depolymerization/decomposition when heated to elevated temperatures thus rendering the propellant less sensitive to spall conditions. Our research is continuing to lower the melt viscosity and increase the elongation of the thermoplastic elastomer.

We have continued research in the area of measuring reactivity ratio of new monomers with the objective of correlating structure versus polymerizability, and have seen that the inclusion of a nitrate ester group on an oxetane ring lowers the propensity of the monomer to polymerize by an order of magnitude over the same substitution by an azido group.

We have extended the series of energetic polymers available for binder applications to include nitrate ester polyether glycols. These new polymers are thermally stable enough for their inclusion into state-of-the-art formulations. They are completely compatible with formulation ingredients and curable by accepted technology. Theoretical performance is significantly increased by use of these polymers with minimal effect on burn rates.

A new generation of thermoplastic elastomers have been synthesized that are processible in the state-of-the-art formulations and equipment. These materials are crystalline segmented block copolymers that undergo sharp

melting characteristics at 85°C and endothermic depolymerization at elevated temperatures. The set thermoplastic elastomers are leathery in nature at ambient temperatures with glass transition temperatures of less than -50°C. Work is in progress to increase the elastomeric nature of these polymers and to decrease the melt viscosity.

IV. EXPERIMENTAL DETAILS

Monomer Synthesis Procedures

The experimental procedures reported below are either new synthesis reactions that are not reported in the open literature, or significantly modified versions of known reactions. All other experiments reported in the text duplicate published procedures.

3,3-Bis(ethoxymethyl) oxetane

Into a 12-liter, five neck flask, fitted with a stirrer, a reflux condenser, and a dry nitrogen inlet tube, 8,000 cc absolute ethanol followed by 717.6 g (31.2 mol) of sodium metal were placed. The temperature was maintained at mild reflux by the use of a cold water bath until all of the sodium had dissolved. To the reaction mixture was then added 1,200 g (7.7 mol) of 3,3-bis(chloromethyl) oxetane and the resultant mixture heated to mild reflux for 24 hours. After cooling to room temperature the reaction products were quenched in 5,000 cc of distilled water, and then extracted with 4 portions of 500 cc methylene chloride. The combined extracts were then dried over magnesium sulfate and the solvent removed by evaporation. Pure monomer was obtained by distillation, the main fraction being collected at 54°C and 1.6 mm pressure. 1,284 g of polymerizable grade monomer were obtained by redistillation from calcium hydride representing a 95% yield.

3,3-Bis(methoxymethyl) oxetane

Into a 12-liter, five neck flask, fitted with a stirrer, a reflux condenser and a dry nitrogen inlet tube, 4,200 cc of anhydrous methanol followed by 552 g (24 mol) of sodium metal were placed. The temperature was maintained at mild reflux by the use of a cold water bath until all of the sodium had dissolved. To the reactor were then added 1,240 g (8 mol) of 3,3-bis(chloromethyl) oxetane and the resultant mixture heated to mild reflux for 48 hr. After cooling to room temperature the reaction products were quenched in 6,000 cc of distilled water, and then extracted with 4 portions of 500 cc methylene chloride. The combined extracts were then dried over magnesium sulfate and the solvent removed by evaporation. Pure monomer was obtained by distillation the fraction boiling at 45°C at 0.3 mm pressure being collected. 1,052 g of polymerizable grade monomer was obtained by redistillation from calcium hydride representing a 90% yield.

3,3-Bis(fluoromethyl) oxetane

Into a 5-liter three neck flask, fitted with a stirrer, and reflux condenser, 1,000 g (17.2 mol) of potassium fluoride suspended in 2,000 cc of anhydrous ethylene glycol were added. To this mixture was then added 1,000 g (6.45 mol) of 3,3-bis(chloromethyl) oxetane and the pot temperature was raised slowly to 180°C. After 1 hour at this temperature the condenser was replaced with a 12-in. vigreaux column and the pot temperature raised to 190°C. The required product was then collected, as formed, from the reactor. After 5 hours 625 g of material was collected and redistillation at a boiling point of 49°C at 155 mm pressure, through a Snyder (floating ball) column, yielded 488 g of product representing a 62% theoretical yield.

3-Hydroxymethyl-3-methyl oxetane

In a 5-liter, round bottom flask fitted with a reflux condenser and an immersion thermometer, 2,007 g (16.7 mol) 1,1,1-trimethylol ethane, 2,000 g (17 mol) diethylcarbonate, and 5 g KOH in 20 cc ethyl alcohol were added. The solution was then heated to reflux at a pot temperature of 111°C. When the pot temperature fell to 100°C the flask was fitted with a vigreaux column and condenser and the ethanol formed allowed to distill off. The distillation was continued until 1,970 cc of ethanol had been collected and the pot temperature was 160°C. At this time the system was connected to a vacuum pump and the pressure reduced until CO_2 was evolved. The pot temperature was maintained at 160°C and the pressure further reduced to maintain a slow distillation with a head temperature of 100° to 110°C. The distillation was stopped when 1,238 g of crude product had been collected. Pure monomer was obtained in 76% yield by redistillation, the fraction boiling at 84°C and 3.5 mm pressure being collected.

3,3-Bis(hydroxymethyl) oxetane

Into a flask equipped with a mechanical stirrer, a thermometer, and a distillation column, a mixture of 272 g (2 mol) of pentaerythritol, 295 g (2.5 mol) of diethyl carbonate, and 0.5 g of sodium metal was added. The reactants were then heated to a pot temperature of 110°C and the ethanol produced was slowly removed by distillation. Ethanol was collected until the pot temperature rose to 140°C at which time a vacuum was applied to remove the final traces of ethanol. An air condenser was then fitted to the reactor

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flask and with careful heating and pressure control the required product was distilled boiling at 125°C and 0.03 mm pressure. 104 g of pure monomer was obtained by redistillation representing a 44% yield.

3-Octoxymethyl-3-methyl oxetane

To a 5-liter, three neck flask, fitted with a reflux condenser, a stirrer, and a dry nitrogen inlet tube, 3,000 cc of p-dioxane and 204 g (2 mol) of 3-hydroxymethyl-3-methyl oxetane were added. To this mixture were then added 47 g (2 mol) of sodium metal and the temperature of the flask raised to reflux temperature. Heating was maintained until all the sodium had dissolved. At this time, 400 g (2 mol) of 1-bromooctane was added and reflux resumed for 3 days. The mixture was then cooled to room temperature and the precipitated sodium bromide removed by filtration. The filtrate was then combined with a large excess of water and extracted with carbon tetrachloride. This solution was further washed with 500 cc distilled water and then dried over magnesium sulfate. The solvent was then removed by evaporation and the required monomer isolated by fractional distillation, the portion boiling at 30°C and 0.3 mm pressure being collected. Redistillation from calcium hydride yielded 190 g of polymerizable grade monomer.

Elemental analysis calculated C, 72.8; H, 12.2
found   C, 72.2; H, 12.6

NMR(CDCL$_3$): δ 0.86 (t, CH$_3$); 1.03 (m, (CH$_2$)$_6$, ring CH$_3$); 3.45 (s,t (CH$_2$OCH$_2$); 4.31, 4.49(ABq CH$_2$OCH$_2$) J=6

3,3-Bis(methoxyethoxymethyl) oxetane

To a 5-liter three neck flask, fitted with a reflux condenser, a stirrer, and a thermometer, were added 1,824 g (24 mol) of 2-methoxyethanol followed by 139 g (6 mol) of sodium metal. The flask temperature was then raised to mild reflux and thus maintained until all the sodium had dissolved. At this time 465 g (3 mol) of 3,3-bis(chloromethyl) oxetane were added and heating maintained for a further 24 hours. The mixture was then cooled to room temperature and the precipitated sodium chloride removed by filtration. The filtrate was dissolved in an excess of water, extracted with 4 portions of 500 cc methylene chloride, and then the combined organic layers dried over magnesium sulfate. The solvent was then removed by evaporation and the required monomer isolated by fractional distillation, the fraction boiling at 85°C and 0.1 mm pressure being collected. Redistillation from calcium hydride yielded 487 g of polymerizable grade monomer.

Elemental analysis calculated C, 56.4; H, 9.4

found   C, 56.1; H, 9.8

NMR(CDCL$_3$) δ 3.36(s, CH$_3$); 3.57(d, OCH$_2$CH$_2$O) J=3; 3.69(s, CH$_2$O); 4.45(s, CH$_2$OCH$_2$)

3-Chloromethyl-3-methyl oxetane

In a 5-liter flask, fitted with a stirrer, condenser, and thermometer, were placed 2,000 cc of carbon tetrachloride. The flask was heated to reflux and then 100 cc of solvent was allowed to distill off and remove any residual water. The flask was cooled to room temperature and to it added 957 g (3.66 mol) of triphenylphosphine and 372 g (3.66 mol) of 3-hydroxymethyl-3-methyl oxetane. The mixture was heated with caution to 65°C, at which point a strong exotherm occurs and the reaction becomes self-sustaining. This exothermic reaction continued for 1 hour at which time external heating was reapplied for an additional 1 hour. The flask was then cooled to room temperature and the resultant precipitate removed by filtration. The filtrate was then dissolved in ether, washed with distilled water, dried over magnesium sulfate, and then evaporated to remove the solvents. Distillation through a Snyder (floating ball) column yielded the required monomer boiling at 64°C and 40 mm pressure. Redistillation yielded 493 g (56%) of polymerizable grade material.

3,3-Bis(nitratomethyl) oxetane

An acetylnitrate solution was prepared by adding and stirring 252 g (4 mol) of 100% nitric acid to 816.8 g (8 mol) of anhydrous acetic anhydride at 20°C. This solution was then cooled to 5°C and added, over a 15 minute period, to a solution of 236 g (2 mol) of 3,3-bis(hydroxymethyl) oxetane in 1,500 cc of methylene chloride at -5°C. After stirring for an additional 15 minutes the reaction was quenched in 672 g of sodium carbonate in 2,000 cc of water. The organic layer was separated and washed with 3 x 2,000 cc portions of distilled water and then dried over magnesium sulfate. The solid product isolated after removal of the solvent was recrystallized from 2,000 cc of carbon tetrachloride. 230 g of the required monomer was obtained (52%) at polymerizable purity, melting point 90 to 92°C.

Elemental analysis calculated C, 28.85; H, 3.85; N, 13.46

found   C, 29.31; H, 3.81; N, 13.29

NMR(CDCl$_3$) δ 4.55(s, CH$_2$OCH$_2$); 4.76(s, CH$_2$O)

3-Nitratomethyl-3-methyl oxetane

An acetylnitrate solution was prepared by adding and stirring 165.4 g (2.6 mol) of 100% nitric acid to 510 g (5 mol) of acetic anhydride at 25°C. This solution was then cooled to 5°C and added, over a 15 minute period, to 255 g (2.5 mol) of 3-hydroxymethyl-3-methyl oxetane in 1,400 cc of methylene chloride cooled to -5°C. After stirring for an additional 15 minutes the contents of the flask were quenched in 700 g of sodium carbonate in 2,500 cc of water. The organic layer was washed with 3 x 2,500 cc portions of distilled water, and then dried over magnesium sulfate. The required product was readily obtained in polymerizable purity by a single pass down a neutral alumina column eluting with 50/50 v/v CHCl$_3$/hexane. The final yield was 242 g of monomer.

Elemental analysis calculated C, 40.82; H, 6.12; N, 9.52

found   C, 40.62; H, 6.06; N, 9.13

NMR(CDCl$_3$) δ 1.38(s, CH$_3$); 4.5,4.37(ABq, CH$_2$OCH$_2$, J=6); 4.6(s,CH$_2$O)

Boiling Point 40°C at 0.1 mm

Polymerization Procedures

Each monomer system requires slightly different polymerization techniques depending on the reactivity ratios of the monomer pairs. Also some

polymerizations are carried out in methylene chloride, or as in the case of polymers containing THF, the polymerization is conducted in bulk (no solvent).

A further technique is used for the block linking of reformed polymers. The following procedures and techniques are general in nature, the actual molecular weights of the polymers produced are only dependent on the stoichiometry of the initiator (BDO/BF$_3$) to monomer ratio and thus are adjusted for a particular synthesis.

Solution Polymerization e.g., BEMO, BMMO, OMMO/BMMO, BFMO/BEMO, BAMO/BNMO, BNMO/NMMO, NMMO, etc.

100 g of calcium hydride dried methylene chloride is charged into a flame dried 500 cc resin flask which is maintained under a nitrogen atmosphere. To this flask is then added the calculated amount of freshly distilled 1,4-butanediol followed by the calculated amount of borontrifluoride etherate (1:2 mol ratio). This solution is allowed to react for 1 hour at room temperature. The reactor is then cooled to -10°C and after 30 minutes a solution of the monomer(s) is added dropwise in methylene chloride (25% w/w concentration). The rate of addition usually ranges from 20 minutes to 2 hours. If the rate of polymerization is unknown then it is followed by GC, until a conversion of >90% is measured. At this time the contents of the flask are quenched with 50 cc of saturated brine solution. The organic phase is separated off, washed with 10% sodium bicarbonate solution, dried over magnesium sulfate and evaporated to dryness at room temperature. The nature of the polymer will dictate the method of purification. In most cases a single precipitation from cold methanol will yield an acceptable polymer.

Bulk Polymerization e.g., BAMO/THF, BFMO/THF, AMMO/THF, BEMO/THF, BMMO/THF, OMMO/THF, BMEMO/THF, etc.

Into a 500 cc flame dried resin flask, which is maintained under a nitrogen atmosphere, is charged a calculated amount of freshly distilled THF. While maintaining the flask at room temperature, a calculated amount of freshly distilled 1,4-butanediol is added followed by a calculated amount of borontrifluoride etherate (the amount of BDO will control the final molecular weight). The flask is then cooled to 0°C and after 60 minutes the calculated amount of the second monomer is added in bulk. The rate of addition is governed by the reactivity ratio of the monomer pair, i.e., if the reactivity

ratio of the second monomer is significantly different (higher) than that of THF then the rate of addition should be slower. The mole fraction of monomer 2 is maintained in the polymerization at a level which will give an apparently idealized copolymerization at the desired monomers-in-polymer composition. If the rate of polymerization is unknown then the polymerization is followed by GC, until a conversion of >90% is measured. At this time the polymerization is quenched, first by the addition of 100 cc of methylene chloride, followed by the addition of 50 cc of saturated brine solution. The organic layer is then separated, washed with a 100 cc sodium bicarbonate solution, dried over magnesium sulfate, and then evaporated to dryness. THF polymers are readily purified by precipitation from cold methanol.

Block Linking Technique

By changing the stoichiometry of the component blocks either A-B-A, $(AB)_n$, or AB-star block polymers may be synthesized.

Example--A-B-A block polymer

Into a 500 cc flame dried resin flask is added a solution of the soft block (BMMO/THF) in dried solvent (benzene, dicloromethane, or tetrachloroethane); the amount of polymer is governed by the equivalent weight of the polymer. A 5 times excess of phosgene is then added while maintaining the flask at 25°C. The normal precautions regarding phosgene should be carefully followed, including placing a KOH trap at the end of the gas/flask train. The formation of the bischloroformate is allowed to continue for 2 hours at which time excess phosgene is removed by passing a stream of dry nitrogen through the flask at slightly elevated temperatures. To this solution is quickly added a solution of the end block at an amount required to end cap the center block. The addition of a HCl scavenger (pyridine, pipyrizine, triethylamine) is normally required for good reaction. At this time the flask is heated to 60°C and an immediate rise in viscosity will be noted. The heating is usually continued overnight. After this time the block polymer can be isolated by precipitation from methanol or water. The final polymer may be reprecipitated from methanol.

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VI. PATENTS, PUBLICATIONS, AND PRESENTATIONS

The following patents were granted, and patent applications filed during this reporting period:

- Cationic Polymerization, U.S. Patent 4,393,199
- Cationic Polymerization, Continuation-in-Part, Application 497,836
- Energetic Copolymers, Application 379,354

The following presentations were made during this reporting period:

- "Recent Advances in the Synthesis of Polymers for Binder Applications," ONR Workshop, University of Massachusetts, 5 April 1983
- "Nitrate Ester Polyether Glycols," ONR Workshop, Chestertown, Maryland, 26 July 1983
- "Novel Polyether Block Copolymers," ONR Workshop, Chestertown, Maryland, 27 July 1983

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Mr. David Siegel
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Code 230
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Dr. Phillip A. Miller
736 Leavenworth St., No. 6
San Francisco, CA 94109

Mr. R. Geisler
ATTN: MKP/MS24
AFRPL
Edwards AFB, CA 93523

Dr. L. H. Caveny
AFO Scientific Research
Director Aerospace Sciences
Bolling AFB
Washington, DC 20332

Mr. Donald L. Ball
AFO Scientific Research
Directorate of Chemical Sciences
Bolling AFB
Washington, DC 20332

Dr. John S. Wilkes, Jr.
FJSRL/NC
USAF Academy, CO 80840

Dr. Richard S. Miller (10)
Office of Naval Research
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Arlington, VA 22217

Dr. R. L. Lou
Aerojet Strategic Propulsion
P.O. Box 15699C
Sacramento, CA 95813

Dr. V. J. Keenan
Anal-Syn Lab Inc.
P.O. Box 547
Paoli, PA 19301

Dr. Philip Howe
Army Ballistic Research Labs
ARRADCOM
Code DRDAR-BLT
Aberdeen Proving Ground, MD 21005

Dr. W. W. Wharton
ATTN: DRSMI-RKL
Commander
U.S. Army Missile Command
Redstone Arsenal, AL 35898

Dr. C. M. Frey
Chemical Systems Division
P.O. Box 358
Sunnyvale, CA 94086

Defense Technical Info Center (12)
DTIC-DDA-2
Cameron Station
Alexandria, VA 22314

Dr. Rocco C. Musso
Hercules Aerospace Division
Allegany Ballistic Lab
P.O. Box 210
Washington, DC 21502

Dr. R. Earl
Hercules Inc. Bacchus Works
P.O. Box 98
Magna, UT 84044

Dr. James H. Thacher
Hercules Inc. Bacchus Works
P.O. Box 98
Magna, UT 84044

Mr. Theodore M. Gilliland
Johns Hopkins University APL
Chemical Propulsion
Johns Hopkins Road
Laurel, MD 20810

Dr. R. McGuire
Lawrence Livermore Lab
Univ of California
Code L-324
Livermore, CA 94550

Dr. R. Rogers, WX-2
Los Alamos Scientific Lab
P.O. Box 1663
Los Alamos, NM 87545

Mr. B. Sobers
Naval Air Systems Command
Code 03P25
Washington, DC 20360

Dr. L. R. Rothstein, Asst Dir
Naval Explosives Dev
Engr Dept
Naval Weapons Station
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Naval Surface Weapons Center
Code R11 - White Oak
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Mr. C. Christenson
Naval Sea Systems Command
Code 62R2
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Mr. L. Roslund
Naval Surface Weapons Center
Code R122 - White Oak
Silver Spring, MD 20910

Professor J. C. Chien
University of Massachusetts
Department of Chemistry
Amherst, MA 03003

Dr. M. J. Kamlet
Naval Surface Weapons Center
Code R11 - White Oak
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Dr. May L. Chan
Naval Weapons Center
Code 3244
China Lake, CA 93555

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Naval Weapons Center
Code 3264
China Lake, CA 93555

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Naval Weapons Center
Code 3244
China Lake, CA 93555

Dr. Karl O. Christe
Rockwell International
6633 Canoga Avenue
Canoga Park, CA 91304

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ATTN: Tech Dir, L. Lofiego
22116 W. Soledad Canyon Rd
Saugus, CA 91340

Mr. M. Stosz
Naval Surface Weapons Center
Code R121 - White Oak
Silver Spring, MD 20910

Mr. Lee N. Gilbert
Naval Weapons Center
Code 3205
China Lake, CA 93555

Dr. E. Martin
Naval Weapons Center
Code 3858
China Lake, CA 93555

Dr. A. Nielsen
Naval Weapons Center
Code 385
China Lake, CA 93555

Dr. R. Reed, Jr.
Naval Weapons Center
Code 388
China Lake, CA 93555

Dr. L. Smith
Naval Weapons Center
Code 3205
China Lake, CA 93555

Dr. A. Faulstich
Chief of Naval Technology
MAT Code 0716
Washington, DC 20360

Strategic Systems Project Office
Propulsion Unit
Code SP2731
Dept. of the Navy
Washington, DC 20376

Mr. E. L. Throckmorton
Strategic Systems Project Office
Dept. of the Navy - Rm 1048
Washington, DC 20376

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Research Triangle PK, NC 27709

Dr. R. F. Walker
USA ARRADCOM
DRDAR-LCE
Dover, NJ 07801

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AFRPL/LKLR
Edwards AFB, CA 93523

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Atlantic Research Corp.
5390 Cherokee Ave.
Alexandria, VA 22314

Dr. Kurt Baum
Fluorochem, Inc.
680 S. Ayon Ave.
Azusa, CA 91702

53

Professor J. H. Boyer
University of Illinois
Dept. of Chemistry
Box 4348
Chicago, IL 60680

Dr. C. Coon
Lawrence Livermore Lab L-329
University of California
P.O. Box 808
Livermore, CA 94550

Aerojet Tactical Systems
ATTN: R. Mironenko
P.O. Box 13400
Sacramento, CA 95813

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Edwards AFB, CA 93523

Commander
AFSC (IGFW)
ATTN: Roger H. Goldie
Andrews AFB, DC 20334

Commander
AFWAL (PORT)
ATTN: Dr. Frank D. Stuil
Wright-Patterson AFB, OH 45433

Commander
AFRPL (MKPB)
ATTN: Mr. Berg B. Goshgarian
Edwards AFB, CA 93523

Dr. Joyce J. Kaufman
The Johns Hopkins University
Department of Chemistry
Baltimore, MD 21218

APPENDIX I

Previously Developed

by

F. Bares,
Analytical Methods Development Section,
Morton Thiokol, Inc.

(a) Determination of Hydroxyl Content in Experimental Polymers Using
the Toluenesulfonyl Isocyanate Method

1.0 TEST DESCRIPTION

A sample of polymer is dissolved in tetrahydrofuran. The hydroxyl is reacted with an excess of toluenesulfonyl isocyanate (TSNCO) to form a sulfonyl carbamate. In a nonaqueous system, this sulfonyl carbamate is acidic and can be titrated directly with tetrabutylammonium hydroxide, after any unreacted TSNCO has been destroyed with water. The endpoint is determined potentiometrically.

2.0 REAGENTS AND APPARATUS

Tetrahydrofuran, stabilized, reagent grade

Isopropanol, reagent grade

Toluenesulfonyl isocyanate solution. Prepare by diluting 10 ml of TSNCO (commercially available from Aldrich or Eastman Chemical Co.) to 250 ml with stabilized tetrahydrofuran. Protect the solution from atmospheric moisture.

Tetrabutylammonium hydroxide (TBAH) solution, 0.1N. Dilute 20 ml of TBAH (25% in methanol, commercially available) to 200 ml with isopropanol.

Automatic titrator, Fisher Titrimeter II AEP or equivalent, equipped with a standard glass combination electrode, or a glass-platinum internal titrant reference electrode combination. In the latter combination, the reference electrode, in the form of a platinum wire insert, is maintained in contact with the titrant through the delivery tip of the titrator.

3.0 STANDARDIZATION OF 0.1N TETRABUTYLAMMONIUM HYDROXIDE

3.1 Weigh, to the nearest 0.1 mg, a 0.2 g sample of benzoic acid into a beaker.

3.2 Add 60 to 80 ml tetrahydrofuran and stir to dissolve.

3.3 Titrate potentiometrically as in Paragraph 4.4.

Calculate the normality of the tetrabutylammonium hydroxide as follows:

$$N = \frac{W}{V \times 0.12212}$$

Where: W = Weight of benzoic acid

V = Volume of TBAH solution (ml)

4.0 PROCEDURE

4.1 Weigh, to the nearest 0.1 mg, approximately 0.2g → 1.2g, to optimize titration conditions, of polymer into a 150 ml beaker. Add 10 ml of tetrahydrofuran and stir to dissolve.

4.2 Add 10 ml of the TSNCO solution, cover the beaker with a watch glass, and let stand for 3 to 5 minutes.

4.3 After the allotted reaction time, add 0.2 ml of distilled water and mix well. Dilute to approximately 100 ml with THF.

4.4 Titrate the sample with 0.1N tetrabutylammonium hydroxide in isopropanol using an automatic titrator equipped with a glass combination electrode or a glass-platinum internal titrant reference electrode combination.

4.5 Run two or more blank determinations as above, eliminating only the sample.

NOTE: The titration curve for samples and blanks will have two breaks.

5.0 CALCULATIONS

$$\text{Hydroxyl Content (eq/100g)} = \frac{(S_2 - S_1) - (B_2 - B_1)}{10W} N$$

Where: S_2 = ml TBAH to titrate to second sample break

S_1 = ml TBAH to titrate to first sample break

B_2 = ml TBAH to titrate to second blank break

B_1 = ml TBAH to titrate to first blank break

N = normality of TBAH

W = weight of sample

Previously Improved and Modified

by

F. Bares,
Analytical Methods Development Section,
Morton, Thiokol, Inc.

(b) Determination of Hydroxyl Content of Experimental Polymers

1.0 TEST DESCRIPTION

A sample is acetylated with a solution of acetic anhydride in pyridine. The excess acetic anhydride is hydrolyzed with water and the resulting acetic acid is titrated with standard potassium hydroxide solution. The hydroxyl content is calculated from the difference in the titration volume of the blank and sample solutions.

2.0 REAGENTS

2.1 ACETYLATING REAGENT. Prepare a 12% v/v solution of acetic anhydride in pyridine in a dry glass stoppered flask. Prepare fresh reagent daily.

2.2 0.5 N POTASSIUM HYDROXIDE IN METHANOL, STANDARDIZED

2.3 PHENOLPTHALEIN INDICATOR, 1% IN ETHANOL

2.4 TEHRAHYDROFURAN, REAGENT GRADE OR $CHCl_3$ AND CH_3OH

3.0 APPARATUS

3.1 FLASKS, ERLENMEYER, 125 ml, WITH GROUND GLASS STOPPERS

3.2 STEAM TABLE

3.3 BURET, 50 ml CAPACITY

4.0 PROCEDURE

4.1 Accurately weigh (to the nearest 0.1 mg) approximately 4 g of sample into a clean dry 125 ml Erlenmeyer flask. Pipet exactly 10 ml of acetylating reagent into the flask. A uniform drainage time must be employed.

4.2 Moisten a glass stopper with pyridine, place the stopper loosely in the flask, and set the flask on a steam table. After heating for approximately two minutes, stopper the flask tightly and heat on the steam table for 2 hours.

4.3 Remove the flask from the steam table and allow to cool for a few minutes. Add 10 ml of distilled water, swirl to mix, stopper loosely and replace the flask on the steam table for 10 minutes.

4.4 Remove the flask from the steam table and allow to cool to room temperature. Add 50 ml of tetrahydrofuran or 40 ml $CHCl_3$-10 ml CH_3OH depending on solubility charactistics, 0.5 ml of phenolpthalein indicator and titrate with standardized 0.5 N potassium hydroxide to the first permanent pink color.

4.5 Perform at least two blank determinations in parallel using the procedure given above, omitting only the addition of sample.

5.0 CALCULATION

$$\text{Hydroxyl content (equivalent/100g)} = \frac{(B-A) \times N}{10 \ W}$$

Where: B = Volume of NaOH to titrate blank (ml)

A = Volume of NaOH to titrate sample (ml)

N = Normality of NaOH

W = Sample weight (g)

3.0 <u>CALIBRATION</u>

3.1 Weigh (to the nearest 0.1 mg) between 0.15 and 0.20 g of monomer into a tared 2-ml volumetric flask.

3.2 Weigh (to the nearest 0.1 mg) approximately 0.10 g of internal standard into the same volumetric flask.

3.3 Dilute to volume with water wet methylene chloride; stopper and shake the solution.

3.4 Inject 1.0 microliters into the gas chromatograph. Push the start button on the integrator and the GC. The following parameters used on the HP 5700 HC provide baseline separation and a reasonable analysis time:

> He Flow Rate: 60 cc/min
> Injection Port Temperature: 150°C
> Oven Temperature: Programmed
>> a. Initial Temperature: 80°C
>> b. Initial Time: 2 min
>> c. Rate: 16°C/min
>> d. Final Temperature: 200°C
>> e. Final Time: 4 min
> Detector Sensitivity: 5 (approximatley 150 MA)
> Column B Attenuation: 2

The settings for the HP 2290A are as follows:
> Attenuation: 0
> Chart Speed: 0.5 cm/min
> Peak Width: 0.04 to 0.16
> Area Rejection: 0

3.5 Make sufficient injections to obtain at least three response factors that agree within 3% of each other, using consecutive injections.

3.6 Calculate the response factor (RF) as follows:

$$RF = \frac{Area_{IS} \times Amount_M}{Area_M \times Amount_{IS}}$$

Where: $Area_{IS}$ = area of the internal standard peak

$Area_M$ = area of the monomer peak

$Amount_{IS}$ = weight of internal standard

$Amount_M$ = weight of monomer

4.0 SAMPLE ANALYSIS

4.1 Weigh (to the nearest 0.1 mg) approximately 1 ml of sample from the polymer reaction flask. This step and the following two steps should be completed as rapidly as possible since the monomer will continue to react in the sample until it is quenched with wet methylene chloride.

4.2 Weigh (to the nearest 0.1 mg) approximately 0.10 g of the internal standard into the same volumetric flask.

4.3 Dilute to volume with water wet methylene chloride, stopper and shake the flask to insure it is well mixed and the reaction quenched.

4.4 Inject 1.0 microliters into the gas chromatograph using the same parameters as were used to analyze the calibration standard.

4.5 Calculate the amount of monomer in the reaction sample aliquot as follows:

$$\text{Weight of monomer} = \frac{(RF) \times \text{Area}_M \times \text{Amount}_{IS}}{\text{Area}_{IS}}$$

Where: RF   = response factor calculated in
                        Paragraph 3.6

   Area_M = area of monomer peak from reaction
                        aliquot

   Amount_{IS} = weight of internal standard added
                        to the reaction aliquot

   Area_{IS} = area of internal standard added to
                        the reaction aliquot

4.6 Calculate the percent monomer left in the reaction using the following equation:

   % monomer left =

   $$\frac{\text{monomer in sample aliquot}}{\text{weight of monomer originally added}} \times 100$$

   Where: The weight of the monomer in the sample aliquot
           was calculated in Paragraph 4.5.

REACTIVITY RATIO PROGRAM

Standardization Calculation

Identify Monomer 1 _____

Identify Monomer 2 _____

Input Number of GC Shots __(3)__

Weight of Standard _____

Weight of Monomer 1 _____

Weight of Monomer 2 _____

Area of Standard in GC Shot 1 _____

Area of Monomer 1 in GC Shot 1 _____

Area of Monomer 2 in GC Shot 1 _____

Area of Standard in GC Shot 2 _____

Area of Monomer 1 in GC Shot 2 _____

Area of Monomer 2 in GC Shot 2 _____

Area of Standard in GC Shot 3 _____

Area of Monomer 1 in GC Shot 3 _____

Area of Monomer 2 in GC Shot 3 _____

Number of Runs at Different Monomer Concentratons _____

Number of Samples Taken Per Run __(1)__

Number of GC Shots Per Sample __(3)__

Molecular Weight of Monomer 1 _____

Molecular Weight of Monomer 2 _____

RUN NUMBER

Weight of Solvent Plus Catalyst	_____
Weight of Monomer 1	_____
Weight of Monomer 2	_____
Weight of Sample Taken	_____
Weight of Standard Added	_____
Area of Standard in GC Shot 1	_____
Area of Monomer 1 in GC Shot 1	_____
Area of Monomer 2 in GC Shot 1	_____
Area of Standard in GC Shot 2	_____
Area of Monomer 1 in GC Shot 2	_____
Area of Monomer 2 in GC Shot 2	_____
Area of Standard in GC Shot 3	_____
Area of Monomer 1 in GC Shot 3	_____
Area of Monomer 2 in GC Shot 3	_____

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0: dim A[7,3,3],B[7,3,3],C[7,3,3],D[3,7],L[7],M[7],N[7],R[7,3]
1: dim S[7,3],A$[30],B$[30];sfg 14;ldk 1
2: dim E[7,3],F[7,3],G[7,3],H[7,3],K[7,3],O[7,3],P[7,3],Q[7,3]
3: dim T[7,3],C$[50]
4: cfg 2;ent "READ DATA FROM A FILE?",I;if flg13=0;sfg 2;gsb "READ"
5: if not flg2;ent "IDENTIFY MONOMER 1",A$,"IDENTIFY MONOMER 2",B$
6: fmt 1,16"*";prt "MONOMER 1 IS",A$,"","MONOMER 2 IS",B$,""
7: if flg2;gto +8
8: "INIT":ent "INPUT # OF GC SHOTS",r0;0→A→B→C
9: ent "WEIGHT OF STANDARD",r5
10: dsp "WEIGHT OF",A$;ent "",r6
11: dsp "WEIGHT OF",B$;ent "",r7
12: fxd 0;prt "# OF GC SHOTS",r0,""
13: fxd 4;prt "WT OF STANDARD",r5,"","WT OF ",A$,r6,""
14: prt "WT OF ",B$,r7,""
15: fxd 0;for I=1 to r0
16: if not flg4;if flg2;gto +7
17: dsp "AREA OF STANDARD IN GC SHOT",I
18: ent "",D[1,I];fxd 0;prt "AREA OF STANDARD","IN GC SHOT",I,D[1,I],""
19: dsp "AREA OF",A$,"IN GC SHOT",I;fmt 2,"AREA OF",c8
20: ent "",D[2,I];wrt 16.2,A$;prt "IN GC SHOT",I,D[2,I],""
21: dsp "AREA OF",B$,"IN GC SHOT",I
22: ent "",D[3,I];wrt 16.2,B$;prt "IN GC SHOT",I,D[3,I],""
23: A+D[1,I]→A;B+D[2,I]→B;C+D[3,I]→C
24: next I
25: (B/A)(r5/r6)→r1
26: (C/A)(r5/r7)→r2
27: if not flg4;if flg2;gto +7
28: ent "RUNS @ DIFFERENT MONOMER CONC.",r8;prt "RUNS @ DIFFERENT"
29: prt "MONOMER CONC.",r8,""
30: ent "SAMPLES TAKEN PER RUN",r9;prt "SAMPLES/RUN",r9,""
31: ent "GC SHOTS PER SAMPLE",r10;prt "GC SHOTS PER","SAMPLE",r10,""
32: dsp "MOL. WT. OF",A$;ent "",r11;prt "MOL. WT OF ",A$,r11,""
33: dsp "MOL. WT. OF",B$;ent "",r12;prt "MOL. WT OF ",B$,r12,""
34: -9999999→r13
35: -r13→r14
36: for I=1 to r8
37: "ANAL":fxd 0
38: fmt 1,16"*";spc ;wrt 16.1;prt "ANAL. FOR RUN",I;wrt 16.1
39: if not flg5;if flg2;gto +7
40: dsp "WT OF SOLVENT+CATALYST IN RUN",I;fxd 0
41: ent "",L[I];prt "","WT OF SOL + CAT","IN RUN",I;fxd 4;prt L[I],""
42: fxd 0;dsp "WT OF",A$,"IN RUN",I;fmt 2,"WT OF ",c10
43: ent "",M[I];wrt 16.2,A$;prt "IN RUN",I;fxd 4;prt M[I],""
44: fxd 0;dsp "WT OF",B$,"IN RUN",I
45: ent "",N[I];wrt 16.2,B$;prt "IN RUN",I;fxd 4;prt N[I],""
46: for J=1 to r9
47: fxd 4
48: fmt 2,"RUN",f2.0,"  SAMPLE",f2.0
49: spc ;wrt 16.2,I,J;if not flg5;if flg2;gto +3
50: ent "WEIGHT OF SAMPLE TAKEN",R[I,J];prt "WT OF SAMPLE","TAKEN",R[I,J],""
51: ent "WEIGHT OF STANDARD ADDED",S[I,J];prt "WT OF STANDARD","ADDED",S[I,J]
52: spc ;0→A→B→C;fxd 0
53: for K=1 to r10
54: if not flg5;if flg2;gto +7
55: dsp "AREA OF STANDARD IN GC SHOT",K
56: ent "",A[I,J,K];prt "AREA OF STANDARD","IN GC SHOT",K,A[I,J,K],""
57: dsp "AREA OF",A$,"IN GC SHOT",K;fmt 2,"AREA OF ",c8
58: ent "",B[I,J,K];wrt 16.2,A$;prt "IN GC SHOT",K,B[I,J,K],""
59: dsp "AREA OF",B$,"IN GC SHOT",K
60: ent "",C[I,J,K];wrt 16.2,B$;prt "IN GC SHOT",K,C[I,J,K],""
61: A+A[I,J,K]→A;B+B[I,J,K]→B;C+C[I,J,K]→C
62: next K
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63: S[I,J]B(L[I]+M[I]+N[I])/r1AR[I,J]→r23
64: M[I]/r11→r24
65: N[I]/r12→r25
66: S[I,J]C(L[I]+M[I]+N[I])/r2AR[I,J]→r26
67: r23/r11→r48
68: r26/r12→r49
69: r24-r48→r50
70: r25-r49→r51
71: r24/(r24+r25)→E[I,J]
72: r25/(r24+r25)→F[I,J]
73: r50/(r50+r51)→G[I,J]
74: r51/(r50+r51)→H[I,J]
75: (r50+r51)/(r24+r25)→K[I,J]
76: fxd 6;wrt 16.1
77: prt "IN. MOLE% A",E[I,J],""
78: prt "IN. MOLE% B",F[I,J],""
79: prt "MOLE% A IN POLY",G[I,J],""
80: prt "MOLE% B IN POLY",H[I,J],""
81: prt "% CONVERSION",K[I,J],""
82: E[I,J]/F[I,J]→X
83: G[I,J]/H[I,J]→Y
84: K[I,J](1+X)/(1+Y)→r27
85: Yr27/X→r28
86: log(1-r28)/log(1-r27)→Z
87: Y/ZZ→O[I,J]
88: (Y-1)/Z→P[I,J]
89: if O[I,J]<r13;gto +2
90: O[I,J]→r13
91: if O[I,J]>r14;gto +2
92: O[I,J]→r14
93: next J
94: if flg5;gto "CHANGES"
95: next I
96: if flg4;gto "CHANGES"
97: ent "CHANGES?",I;if flg13=0;gsb "CHANGES"
98: √(r13r14)→r29
99: for I=1 to r8
100: for J=1 to r9
101: O[I,J]/(r29+O[I,J])→Q[I,J]
102: P[I,J]/(r29+O[I,J])→T[I,J]
103: r30+Q[I,J]→r30
104: r31+T[I,J]→r31
105: r32+Q[I,J]↑2→r32
106: r33+T[I,J]↑2→r33
107: r34+T[I,J]Q[I,J]→r34
108: next J
109: next I
110: r8r9→A
111: (Ar34-r30r31)/(r32A-r30↑2)→r35
112: (r31-r35r30)/A→r36
113: (r34A-r30r31)↑2/(r32A-r30↑2)(r33A-r31↑2)→r37
114: prt "CORR COEF",√r37
115: -r36r29→r4
116: r35+r36→r3
117: prt "R1=",r3,"R2=",r4
118: Ar32-r30↑2→r38
119: √(r33A-r31↑2-r38r35↑2)/√((A-2)A)→r39
120: r39√(A/r38)→r40
121: r39√(r32/r38)→r41
122: √(r41↑2+r40↑2)→r42
123: √((-r29r41)↑2)→r43
124: prt "DEV IN R1="," +/-",r42
125: prt "DEV IN R2="," +/-",r43
126: ent "STORE DATA?",I;if flg13=0;gsb "RECORD"
127: ent "PLACE PAPER IN PLOTTER, HIT CONT",I
128: cfg 1;gsb "GRID"
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195: if r57-r56>=10;.1r57+r57;.1r56+r56;sfg 3
196: (int(10r56)-1)/10+r52
197: if r56<0;(10r56+frc(10r56)-1)/10+r52;int(10r52)/10+r52
198: (int(10r57)+1)/10+r54
199: 0+r53;1+W
200: "INT":for I=5 to 9
201: if frc(10(r54-r52)/I)=0;(r54-r52)/I+r53
202: next I
203: if r53=0;.1W+r(53+W)+r(53+W);-1W+W;gto "INT"
204: frc(r54/r53)+r55;if r55=0;gto +3
205: if r55<.5;r54-r55r53+r54;r52-r55r53+r52;if r57>r54;r54+r53+r54
206: if r55>=.5;r54+r55r53+r54;r52+r55r53+r52;if r56<r52;r52-r53+r52
207: if flg3;10r52+r52;10r53+r53;10r54+r54
208: ret
209: "ETA-XI":wrt 705,"IP1740,3025,6550,7920"
210: scl 0,1,r52,r54;wrt 705,"TL2";wrt 705,"VS";csiz 1.5,1.5
211: xax r52,.1,0,1;fxd 1;for I=0 to 1 by .1
212: plt I,r52,1;cplt -2,-1;lbl I
213: next I
214: yax 0,r53,r52,r54,1;csiz 2,1.5
215: wrt 705,"TL0,2";xax r54,.1,0,1;yax 1,-r53,r54,r52
216: plt .5,r52,1;cplt -1,-2;lbl "Xi"
217: csiz 2,1.5,1,90;plt 0,r52+(r54-r52)/2,1;cplt -1.5,2;lbl "Eta"
218: "Eta VS Xi PLOT FOR "+C$;A$+C$[len(C$)+1]
219: "/"+C$[len(C$)+1];B$+C$[len(C$)+1]
220: csiz 2.5,1.5;plt .5,r54,1;cplt -len(C$)/2,2;lbl C$
221: csiz 1.5,1.5;fxd 3;plt .6,r52,1;cplt 0,2;lbl "ALPHA=",r29
222: ret
223: "SYMB":plt Q[I,J]+.0075,T[I,J],1
224: for L=0 to 360 by 20
225: plt Q[I,J]+.0075cos(L),T[I,J]+.0075(r54-r52)sin(L),2
226: next L
227: plt Q[I,J],T[I,J],1
228: ret
229: "CHANGES":
230: ent "CHANGE INITIAL PARAMETERS?",I;if flg13=0;sfg 2,4;gto "INIT"
231: cfg 4
232: ent "CHANGE PARAMETERS FOR A RUN?",I;if flg13;ret
233: sfg 5,2;ent "RUN #?",I;gto "ANAL"
234: cfg 5;ret
*4970
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